

Carbon and Nitrogen Mineralization in Wetland Soils of the Canadian Prairies

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By

Christian D. Dedzoe

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ABSTRACT

Wetland soils form an integral part of the agricultural hummocky landscape in the Canadian Prairies. These soils sequester carbon and can serve as sources of greenhouse gases. Three distinctly different but contiguous soils – Humic Luvic Gleysols (HLG), Eluviated Dark Brown Chernozems (EDBC) and Calcareous Dark Brown Chernozems (CDBC) – located in the St. Denis National Wildlife Area (SDNWA) in four wetlands were selected for study with the aim of comparing the carbon (C) and nitrogen (N) mineralization parameters and determining soil-related factors that influence C and N mineralization in these soils. A short-term aerobic incubation study (16 d) was conducted to determine C mineralization. Nitrogen mineralization was examined using two soil N availability indices: nutrient supply rate (NSR) in a short-term incubation study (14 d) and aerobic leaching-incubation in a long-term study (16 wk). A first order model using non-linear least squares regression was fitted to cumulative C and N curves to determine C and N mineralization parameters (C mineralization potential, C_o and C mineralization rate constant, k_C ; N mineralization potential, N_o and N mineralization rate constant, k_N) for each soil type. Mean cumulative C mineralization, C_o , mean cumulative N mineralization and N_o were highest in the surface horizons and decreased with depth in all the soils. The mean cumulative CO_2 production values for the surface horizons were $> 150 \text{ mg } CO_2\text{-C kg}^{-1} \text{ soil}$ while the lower horizon values were $< 80 \text{ mg } CO_2\text{-C kg}^{-1} \text{ soil}$. Surface mean cumulative N mineralization values were between $5 \text{ mg N kg}^{-1} \text{ soil}$ and $10 \text{ mg N kg}^{-1} \text{ soil}$ with the lower horizons being $< 5 \text{ mg N kg}^{-1} \text{ soil}$. The pattern was similar for C_o and N_o in the surface horizons with values ranging from $200 \text{ mg } CO_2\text{-C kg}^{-1} \text{ soil}$ to $> 300 \text{ mg } CO_2\text{-C kg}^{-1} \text{ soil}$ and from $8 \text{ mg N kg}^{-1} \text{ soil}$ to $28 \text{ mg N kg}^{-1} \text{ soil}$, respectively. Nutrient supply rate also showed a similar pattern. The clay fraction showed a stronger negative correlation with the C mineralization parameters in the CDBC than in the other two soils. Organic C and N showed a highly significant positive correlation with almost all the mineralization parameters in all the soils. Overall, notwithstanding the differences in pedogenetic characteristics of the three soils, few significant differences were observed when their C and N mineralization assays were compared. The similarity in the biochemical characteristics of the soils suggests that the observed pedogenic differences do not reflect significantly in the C and N mineralization. Although the pedogenic differences are large, the effects of these differences on soil management are not agronomically significant and the soils can be managed together.

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TABLE OF CONTENTS

| | |
|--|-----|
| PERMISSION TO USE | i |
| ABSTRACT | ii |
| ACKNOWLEDGEMENTS | iii |
| TABLE OF CONTENTS | iv |
| LIST OF TABLES | vi |
| LIST OF FIGURES | vii |
| 1.0 INTRODUCTION | 1 |
| 2.0 LITERATURE REVIEW | 3 |
| 2.1 Wetlands | 3 |
| 2.1.1 <i>Types of wetlands in Canada</i> | 3 |
| 2.1.2 <i>Evolution of Prairie Wetlands</i> | 4 |
| 2.1.3 <i>Wetland hydrology</i> | 4 |
| 2.1.4 <i>Wetland soils and sediments</i> | 5 |
| 2.2 C and N mineralization | 8 |
| 2.2.1 <i>Factors controlling C and N mineralization</i> | 8 |
| 2.2.2 <i>Carbon mineralization</i> | 11 |
| 2.2.2.1 <i>C dynamics in the Prairies</i> | 11 |
| 2.2.2.2 <i>Assessing soil C availability</i> | 14 |
| 2.2.3 <i>Nitrogen mineralization</i> | 15 |
| 2.2.3.1 <i>Assessing N availability</i> | 16 |
| 3.0 C AND N MINERALIZATION IN WETLAND SOILS OF THE CANADIAN PRAIRIES | 22 |
| 3.1 Introduction | 22 |
| 3.2 Materials and methods | 24 |
| 3.2.1 <i>Study site</i> | 24 |
| 3.2.2 <i>Land use history</i> | 24 |
| 3.2.3 <i>Research design and soil sampling strategy</i> | 24 |
| 3.2.4.1 <i>Sample preparation and nitrogen supply rate (NSR) determination</i> | 25 |
| 3.2.3.2 <i>Determination of nitrogen mineralization potential (N_o)</i> | 27 |
| 3.2.4 <i>Laboratory methods</i> | 27 |

| | | |
|-------|--------------------------------------|----|
| 3.2.5 | <i>Data analyses</i> | 28 |
| 3.2.6 | <i>Calculations</i> | 30 |
| 3.3 | Results | 32 |
| 3.3.1 | <i>Soil properties</i> | 32 |
| 3.3.2 | <i>Carbon mineralization</i> | 34 |
| 3.3.3 | <i>Nitrogen dynamics</i> | 41 |
| 3.4 | Discussion | 47 |
| 3.5 | Conclusions and Recommendations..... | 55 |
| 4.0 | REFERENCES | 57 |
| 5.0 | APPENDICES | 71 |

LIST OF TABLES

| | | |
|-------------|--|----|
| Table 3.1: | Particle size distribution in horizons of three wetland soils..... | 32 |
| Table 3.2: | Distribution of some chemical properties in horizons of three wetland soils..... | 34 |
| Table 3.3: | Total C mineralization, mean potential C mineralization, C mineralization rate, mineralization rate constant and initial potential mineralization rate..... | 36 |
| Table 3.4: | Normalized C mineralization parameters with soil OC..... | 38 |
| Table 3.5: | Pearson's correlation coefficient between C mineralization parameters and soil horizon properties..... | 39 |
| Table 3.6: | Pearson's correlation coefficient between C mineralization parameters and soil properties..... | 39 |
| Table 3.7: | Nutrient supply rate using plant root simulator (PRS TM) probes..... | 41 |
| Table 3.8: | Total N mineralization, mean potential N mineralization, N mineralization rate, mineralization rate constant and initial potential mineralization rate..... | 43 |
| Table 3.9: | Normalized N mineralization parameters with soil N..... | 44 |
| Table 3.10: | Pearson's correlation coefficient between N mineralization parameters and soil horizon properties..... | 45 |
| Table 3.11: | Pearson's correlation coefficient between N mineralization parameters and soil properties..... | 45 |

LIST OF FIGURES

| | | |
|-------------|--|----|
| Figure 2.1: | Classical versus more realistic models concerning N mineralization..... | 17 |
| Figure 3.1: | Mean horizon thickness for three soil classes and mean position for 15-cm sampling increments for horizon-based sampling..... | 25 |
| Figure 3.2: | Mean cumulative CO ₂ production in three wetland soils..... | 35 |
| Figure 3.3: | Mean cumulative N mineralization in three wetland soils..... | 42 |

1.0 INTRODUCTION

Carbon (C) is an important element that affects the Earth's ecological systems, particularly influencing the variability in its climate over decades. Estimates show that the quantity of C stored in the soil is two times the amount in the atmosphere and three times that in aboveground biomass. Soil C stock is an important link in the biogeochemical cycling of C thus it is necessary to take soil C into consideration in studies involved with C budgets on a global scale (Wilding et al., 2001). Globally, wetland ecosystems are known to accumulate organic matter in soil and are more effective in soil C storage than other ecosystems because organic matter decomposition is slow under saturated and anaerobic soil conditions (Adhikari et al., 2009). Therefore, estimating the magnitude and potential mineralizability of C reserves in soils, particularly those in wetlands, will provide information on the nutrient supplying capacity of these soils.

Like C, nitrogen (N) is an important nutrient element in the environment. Availability of N can limit the productivity of terrestrial and aquatic ecosystems with low N supplying power. Additionally, its accumulation in high amounts in the soil and subsequent emission as nitrous oxide (N_2O) is a source of environmental concern, particularly with respect to global warming (IPCC, 2001). Transformation of organic N by heterotrophic microorganisms is the primary mechanism for producing inorganic N (as ammonium $[\text{NH}_4^+]$ and nitrate $[\text{NO}_3^-]$). Not only is this inorganic N pool a significant source of N for plant and microbial use, but it can also be a significant source of environmental contamination.

The linkages between C and N biogeochemical cycles are through organic matter transformation, N assimilation, N mineralization and denitrification (Yano et al., 2000). This makes the C and N ratio (C:N ratio) an important indicator of N availability and also a determinant of organic matter source in ecosystems. The N supplying power of soils can be estimated by using soil N availability indices such as nutrient supply rate (NSR) using ion exchange membranes, which assess the cation and anion supplying capacity of soils (Qian and Schoenau, 2002) and potentially mineralizable N which involves incubation and leaching under aerobic or anaerobic conditions (Campbell et al., 1981).

A century of research on agricultural land has yielded a great deal of information about C and N mineralization in the Canadian Prairies. During the past century there has been considerable clearing of wetlands in agricultural landscapes and the incorporation of these former wetlands into agricultural fields. However, the C and N dynamics of these wetland soils are still poorly understood, in part because the level landscapes typically used in classical small-plot research do not include wetlands.

The wetlands in the Canadian Prairies include a number of major soil classes and the origin of some of these classes remains obscure. For example, over two decades of research in these wetlands have led to the identification of a wetland soil informally named *gyttja* by wetland scientists. This soil often has a black colour, which gives the impression that it may contain large reserves of organic carbon, and hence may be presumed to be very fertile for crop production. Since this soil and other soils in the wetlands of the Prairies form part of the agricultural landscape, it is necessary to examine their C and N mineralization potentials and also determine what factors influence the mineralization in these wetland soils in the Prairies.

The objectives of this study were to:

- compare C and N mineralization attributes of wetland soils within the agricultural fields of the Prairies; and
- identify soil-related factors that influence C and N mineralization in these soils.

2.0 LITERATURE REVIEW

2.1 Wetlands

Wetlands are areas of the landscape where water covers the soils or is present either at or near the soil surface or within the root zone of plants throughout the year or for varying periods during the year, including the growing season (Price et al., 2005). In Canada, wetlands occupy approximately 26% of the combined land area of the Prairie provinces (Alberta, Saskatchewan and Manitoba) (Zoltai, 1988). Two major wetland zones are identified in these provinces, which fall within the prairie pothole region (PPR) of North America. In the southern section of each province is the grassland-parkland zone dominated by marshes and shallow freshwater and saline ponds (Kuhry et al., 1992). Occurring in the northern sections of these provinces is the boreal zone with its characteristic peatlands. The grassland-parkland type, with its distinct and numerous potholes, forms an integral part of agricultural fields in the Prairie provinces, which has promoted their conversion into farmlands.

2.1.1 Types of wetlands in Canada

Based on physical and chemical properties, five wetland types are recognized in the Canadian wetland classification system: marshes, swamps, bogs, fens and areas of shallow open water (Zoltai, 1988). Marshes are wetlands that are usually submerged in water and are characterized by the presence of non-woody plants. They are fed mostly with surface water though some may also receive groundwater, and are slightly acidic to alkaline. Common types of marshes are the prairie potholes also referred to as depressional wetlands (Leibowitz and Nadeau, 2003) which dominate the PPR of North America. Swamps are dominated by woody vegetation with the vegetation being either shrubby or forested. They have similar chemical characteristics as marshes. Bogs and fens develop as peatlands and are broadly classified as organic wetlands. However, bogs receive their water supply mainly from precipitation and they are very acidic whereas fens are fed through drainage from the surrounding upland soils and from groundwater. Fens are less acidic and contain more nutrients than bogs. In the Canadian Wetland Classification System, marshes, swamps and areas of shallow open waters are broadly referred to as mineral wetlands, and fens and bogs as organic wetlands (Warner and Rubec,

1997). Together, marshes, swamps, fens and bogs are also known as palustrine wetlands because they do not experience tidal or wave-action, while areas of shallow open waters, characterized by the presence of aquatic macrophytes which float on the water surface and show tidal or wave action are also known as lacustrine wetlands (Cowardin et al., 1979; Warner and Rubec, 1997).

2.1.2 Evolution of Prairie Wetlands

Many studies on wetland soils and sediments in the prairies have centered on Holocene paleoenvironmental reconstruction by using such proxies as mineralogy and lithostratigraphy (Last and Sauchyn, 1993; Last and Vance, 2002), pollen and organic matter (Sauchyn, 1990; Sauchyn and Sauchyn, 1991), ostracode records (Porter et al., 1999), diatoms (Laird et al., 1996) and plant macrofossils (Yansa, 1995; 1998). These studies typically show that wetlands in the Prairies have undergone significant environmental change throughout the Holocene and hence the legacy of these past environments on soil distribution may be major. Of particular interest in this study are events during the Holocene which was characterized by deglaciation, shaping of the land surface and development of drainage basins. The early Holocene, which occurred from 11,000 to 7500 yr before present (BP), is marked by deposition of materials as a result of melting ice. The period was followed by the mid-Holocene, referred to as hypsithermal in the northern hemisphere, and lasted from 7500 to 4000 yr BP. The hypsithermal was a period of warm and dry climatic conditions and full of eolian activity especially in the Great Plains region of North America (Miao et al., 2007). This also changed the landscape tremendously with large deposits of loess material which mantled the original landscape. The late Holocene period occurring from 4000 yr BP to present has been generally cool and wet (Polyak et al., 2001).

2.1.3 Wetland hydrology

Wetland hydrology, particularly in the PPR, is classically modeled on the flow systems of local groundwater patterns. On this basis, three main types of wetlands are identified; namely recharge, throughflow and discharge (Richardson and Brimson, 2001; Euliss et al., 2004; Van der Kamp and Hayashi, 2009). Recharge wetlands occur above the groundwater in the landscape, consequently water flows from them into the groundwater. Their main source of

water is precipitation which they receive as snowmelt with little from the surrounding catchment (Mitsch and Gooselink, 2000). Discharge wetlands, on the other hand, experience water additions from groundwater and therefore are, fed with water from it in addition to precipitation and overland flow. Throughflow wetlands occupy intermediate positions between recharge and discharge wetlands in the landscape, with water flowing laterally across the wetland (Richardson et al., 1992; Richardson et al., 2001).

As water moves through recharge wetlands into the groundwater, it leaches soluble materials and also translocates clay deeper into the soil (Miller et al., 1985). In the case of discharge wetlands, soluble materials are brought up with the water, which evaporates and leads to precipitation of these materials either on the soil surface or in the top layers. Apart from this well-known model of wetland hydrology, studies in parts of the PPR such as St. Denis National Wildlife Area (SDNWA) have shown that water moves laterally towards wetland fringes in response to reduced hydraulic conductivity with depth (Hayashi et al., 1998). According to Hayashi et al. (1998) this flow direction is induced by transpiring plants at the wetland fringes. Other studies in the PPR also have found surface water movement from wetland to wetland through a process termed temporal connectivity (Leibowitz and Vining, 2003). In this process, water spills over from upslope wetlands which have more water than their storage capacity into other wetlands at lower elevations.

2.1.4 Wetland soils and sediments

Many studies on current wetland soils have focused on the soil and hydrological interactions of these soils. Some of these studies examined the hydrology of isolated wetlands (Leibowitz and Nadeau, 2003; Winter and Labaugh, 2003), the role of wetlands in groundwater recharge (Berthold et al., 2004), the relationship between wetland hydrology and dissolved organic carbon (Waiser, 2006) and geochemical processes in recharge wetlands (Heagle et al., 2007). One significant study examining the influence of groundwater on soil formation in the Canadian prairies revealed that runoff inflow into the soils is the major factor controlling salt distribution in them, and this also contributed to the deep profiles of the soils and their high clay contents (Miller et al., 1985). The soils fall under the Gleysolic order of the Canadian System of

Soil Classification based on the presence of redoximorphic features, which indicate that the soils have experienced fluctuating or prolonged periods of wetness (Soil Classification Working Group, 1998). The soils were classified as Luvic Gleysols at the great group level due to the presence of clay-rich horizons in the subsoil, which is indicative of accumulation of illuvial clay designated as Btg. At the subgroup level they are called Humic Luvic Gleysols based on the surface horizon (Ah or Ap) having a darker color than the underlying B horizon as a result of higher organic matter (or carbon) levels. Similar soils were also observed by Bedard-Haughn and Pennock (2002) in the hummocky landscape at St. Denis National Wildlife Area (SDWNA) in Saskatchewan. They termed these depressional soils as Gley Recharge soils with characteristic gley features, eluvial and clay-rich horizons. Other studies also observed the high clay contents of these depressional soils and sediments (Pennock and Vreeken, 1986).

A second major group of soils results from the lateral discharge of pond water into the soils surrounding the wetlands, as discussed in the section above. As the water is lost through evaporation and transpiration, the concentration of solutes increases and ultimately precipitation minerals like calcite, gypsum, and a range of more soluble salts may occur (Miller et al. 1985; Bedard-Haughn and Pennock, 2002). Studies on the mineralogy and isotopic composition of the carbonate minerals have shown that the carbonates in these soils are primarily of pedogenic origin (Wang and Anderson, 2000; Landi et al., 2003b). If these soils are dominated by re-precipitation of carbonate minerals they are classified as either Calcareous or Rego subgroups of the Chernozemic order; if they are dominated by more soluble salts they are classified as saline phases of the Chernozemic, Gleysolic, or Regosolic orders (Miller et al., 1985).

A final group of wetland soils commonly found in the Prairies is poorly understood at this time. These soils have layers at or close to the surface that are typically well sorted silty clays that often show distinct horizontal laminations (Yansa, 1998; Dean and Schwalb, 2000). The sediments are initially black but upon exposure to the atmosphere their colour changes from black to light gray. The layers range in thickness from 10 cm to several metres thick, and in some cases have paleosols interspersed with the sediment (Pennock and Vreeken, 1986; Yansa, 1998; Bedard-Haughn and Pennock, 2002). These layers were labeled as a coprogenous layer (Cco) in Bedard-Haughn et al. (2006) and have been informally referred to as *gyttja* (a Swedish term for

sticky wet and viscous substance). Lithologically, these sediments also have been described as lacustrine silty clays comprising some laminations (Yansa, 1998; Dean and Schwalb, 2000) and, in some cases, they show indistinguishable beddings (Last and Vance, 2002).

These sediments develop under fluctuating oxic and anoxic conditions and show characteristic morphological and chemical properties as a result of long periods of water saturation. These fluctuating conditions result in the reduction, translocation and/or oxidation of iron and manganese compounds to give the sediments morphological characteristics known as redoximorphic features (Vepraskas, 2001). The main redoximorphic features of these unique sediments are redox concentrations, redox depletions and reduced matrix which is the result of reduction, translocation and/or oxidation of iron and manganese compounds. Redox concentrations are formed when reduced iron and manganese move to aerated zones in the soil and precipitate. The precipitate accumulates over time to produce redox concentrations. The reverse of this process yields redox depletions, which may occur in two forms. In one type, iron (and to some extent manganese) is dissolved and lost from some parts of the soil. This is known as iron depletion. The second type is referred to as clay depletions and differs from iron depletions by being the product of both loss of iron and clay with the eventual soil texture becoming coarser than the original matrix texture. Reduced matrices are formed when iron (III) is reduced to iron (II) thus giving the soil matrix a gray color (Vepraskas, 2001). This process is reversible and when the soil is exposed to air or becomes aerated the color changes to yellow or red. Formation of the above features depends on the dynamics of a wetland's hydrology.

In smaller depressions the hydroperiod (or period of inundation) is shorter and the redoximorphic features are only weakly expressed (Miller et al., 1985). Based on horizon designation and characteristics described by the Soil Classification Working Group (1998) these soils exhibit coarse-textured Ae horizons overlying higher clay Bt horizons (or in some cases Btgj horizons) as a result of translocation of clay particles (Schaetzl and Anderson, 2005). The soils are classified as either Chernozemic soils of the Eluviated subgroup, or (if the redoximorphic features are strongly expressed) of the Gleyed or Gleyed Eluviated subgroups (Soil Classification Working Group, 1998). These will be grouped as Eluviated subgroup soils for the remainder of the thesis.

2.2 C and N mineralization

Although there are major differences in the pedology of the three groups of wetland soils, it is less clear if these pedological differences lead to differences in the optimum management of these soils. One of the key aspects to management is the difference in C- and N-cycling associated with the three classes of soils. For both greenhouse gas production and agronomic implications, the differences in C and N mineralization are especially critical.

The conversion of organic matter (OM) into inorganic compounds through decomposition reactions by microorganisms is termed mineralization (Gregorich et al., 2001). Two major products of the mineralization process are CO₂, which results from microbial respiration (Hopkins, 2008) and mineral N (Curtin and Campbell, 2008). Numerous studies have been carried out to determine the C and N mineralization potential of soils, and this section reviews some of them.

2.2.1 *Factors controlling C and N mineralization*

Soil organic matter is the main reservoir of major nutrients including N and as such mineralization of C and N is essential for the maintenance of ecosystem functions, particularly agricultural production and its sustainability. The turnover from this process, however, depends on a number of factors such as the quality of OM added to the soil and other environmental factors.

The quality of OM affects the rate of decomposition (Troeh and Thompson, 2005; Brady and Weil, 2008b). One of the means of assessing OM quality is in terms of the C:N ratio. The C:N ratio provides an index for determining the turnover period of N to the soil (Booth et al., 2005; Brady and Weil, 2008b) so when OM with wide C:N ratio is added to the soil mineralization typically is delayed (Mack and D'Antonio, 2003). However, as decomposition continues the C:N ratio narrows with more N turnover per C mineralized (Hirobe et al., 2003). Organic matter quality is also determined in terms of its lignin:N and polyphenol:N ratios. Organic matter is considered high quality when it has narrow levels of these ratios because OM will decompose easily and with high N mineralization rates (Vanlauwe et al., 1996; Raiesi,

1998). The management of OM is also a factor that can affect microbial activity and population (Chander et al., 1997; Islam and Weil, 2000), soil moisture and the distribution of nutrients in the soil (Islam and Weil, 2000; Lobe et al., 2001).

The main soil related properties that affect mineralization are texture, pH and mineralogy. Soil texture, especially the dominant particle size fraction, plays numerous roles that affect C and N mineralization. Soils with high clay content tend to stabilize and protect SOM from microbial decomposition (Feller and Beare, 1997; Baldock and Skjemstad, 2000). Decomposition usually takes place in well aerated pore spaces. This means soils with large pores (sandy soils) will enhance C and N mineralization while those with small pore sizes (clayey soils) will suppress the process (Franzluebbers, 1999; Baldock and Skjemstad, 2000). Clay content also enhances aggregation of the different particle size fractions that protect OM from microbial attack (Gale et al., 2000; Six et al., 2002).

Generally, the extent of protection offered to the SOM increases in proportion with silt and clay content of the soil (Six et al., 2002). Stabilization of SOM with clay is enhanced by its adsorption onto the charged surfaces of the clay (with colloidal properties as SOM). Another reason for the stabilization of OM conferred by clay is the location of SOM in small pores of numerous microaggregates present in clay where SOM is offered physical protection from microbial decomposition (Gregorich et al., 1989).

The presence of polyvalent cations in the soil solution also provides a protective mechanism for SOM. Soils with high levels of Ca^{2+} , Al^{3+} and Fe^{3+} tend to store more C thus stabilizing it and preventing it from decomposing (Hassink et al., 1997; Baldock and Skjemstad, 2000; Six et al., 2002). Calcium is known to be a strong stabilizing agent for SOM and at whatever stage of decomposition, Ca^{2+} sequesters SOM in a carbonate film (Schaetzl and Anderson, 2005).

Among the models proposed to depict SOM stabilization by soil aggregates is the classical one by Edwards and Bremner (1967) which shows how soil microaggregates protect SOM:

$$\text{Microaggregate} = [(\text{Cl-P-OM})_x]_y \quad [\text{Eq. 1}]$$

where Cl = clay particle;

P = polyvalent cation (e.g. Fe^{3+} , Al^{3+} , Ca^{2+} and/or Mg^{2+})

OM = organic molecule and X and Y are the number of these units bonded together to form a microaggregate.

In the microaggregate, clay particles are linked to organic material by polyvalent cations on exchange sites leading to stabilization of SOM (Edwards and Bremner, 1967). Thus microaggregation offers physical protection to SOM against microbial attack and hence it is not mineralized. However, destruction of the microaggregates promotes mineralization (Gregorich et al., 1989).

Other environmental factors that influence C and N mineralization are temperature and moisture. The rate of biochemical reactions such as mineralization increases with increasing temperature. Studies have documented that C and N mineralization increase as temperature is increased (MacDonald et al., 1995; Leiros et al., 1999). The increase in mineralization, in response to the temperature increase, is expressed as the Q_{10} factor, which shows the rate at which a reaction increases when the temperature is increased by 10 °C (Smith et al., 2003). Most biochemical reactions including mineralization have a Q_{10} factor of 2 over the temperature range from 10 to 30 °C (Griffin, 2008). Moisture also exerts a significant influence on C and N mineralization because all biochemical reactions occur in the medium of water. Though mineralization can occur within a wide range of moisture levels, when the soil dries microbial activity is restricted and hence mineralization typically is reduced (Rey et al., 2002). On the other hand, excess moisture occupies pore spaces, reduces aeration and creates anaerobic conditions which also suppresses mineralization (Smith et al., 2003). Just like temperature, mineralization increases with increases in moisture content up to an optimum of about 60% water-filled pore space (WFPS) (Linn and Doran, 1984; Sierra, 1997; De Neve and Hofman, 2002). Values of WFPS above this optimum create anaerobic conditions resulting in reduced

mineralization and increased denitrification because the soil pores become saturated with water thus limiting oxygen supply (Weier et al., 1993). Temperature and moisture are, therefore, important environmental factors that affect C and N mineralization in soils.

Soil pH also effects C and N mineralization. Generally, near-neutral pH values are optimal for enhanced mineralization. Values on either side of neutrality restrict microbial activity and growth and consequently suppress mineralization (Weier et al., 1993).

The type of clay mineral present also affects C and N mineralization. The clay minerals have varying cation exchange capacity (CEC) and specific surface areas and hence will adsorb SOM to varying degrees. The 2:1 clay minerals such as smectite have relatively high CEC and tend to adsorb high amounts of SOM and protect it from microbial attack, while the 1:1 clay minerals such as kaolinite with their low CEC adsorb less (Six et al., 2002). As a result C and N mineralization will be higher in the latter than the former.

2.2.2 Carbon mineralization

2.2.2.1 C dynamics in the Prairies

The prairies are known to have large reserves of soil organic carbon (SOC) in the agricultural lands of Canada (Smith et al., 2009). The SOC store varies according to soil type ranging from 80 Mg ha⁻¹ in the Brown to 150 Mg ha⁻¹ in the Black soil zones (Landi et al., 2003a). However, over the years, intensive crop production has negatively affected the fertility status of these soils. This negative effect results from the cultivation-induced increases in mineralization rates due to changes in soil temperature and moisture regimes. The goal of some current forms of soil management, such as conservation tillage, is to sequester more C through the exploitation of biological processes within these soils so as to improve soil productivity.

Addition of organic materials to the soil and their subsequent transformation plays a significant role in C-cycling. Through the transformation process C becomes easily dispersed and stabilized in the soil by prompting soil aggregation and being sorbed onto mineral surfaces (Grandy and Neff, 2008). In the absence of stabilization, mineralization by microorganisms

takes place. Carbon mineralization is the process of converting organic materials such as plant and animal biomass into CO₂, as a result of microbial respiration, with subsequent evolution of the gas from the soil. Organic materials that are not mineralized build up as soil humus and contribute to C storage by the soil. These changes are therefore a reflection of biological activity and mineralogy of the soil particles (Sollins and Spycher, 1983).

In the Canadian Prairies, the clay mineralogy of the soils is obtained from the underlying rocks with little variability (Kodama, 1979). The dominant clay minerals are smectite and mica, while kaolinite, chlorites and vermiculites can also be found in smaller amounts. Smectites are highly reactive and are particularly active in binding with SOM and preventing its decomposition.

Calcium is the main polyvalent cation in the wetland soils for binding to SOM. As discussed above, high CaCO₃ discharge soils are commonly found around the edge of wetlands in the PPR. Studies by Landi et al. (2003b) showed that Rego Black soils on calcareous parent materials stored more SOC (210.2 Mg C ha⁻¹) than Black soils (148.8 Mg C ha⁻¹). They attributed this to stronger bonding of OM with carbonates, particularly with the Ca²⁺, in the Rego Black soils than in the Black soils. According to Duchaufour (1976), carbonates being strong stabilizing agents, can sequester fresh or decomposed OM without transforming or polymerizing it, thus increasing the C storage capacity of soils with high carbonate contents.

Carbonate minerals can be lithogenic (inherited from parent material) or pedogenic (secondary) in origin. The main carbonate minerals in the Canadian Prairie soils are dolomite and calcite (Wang and Anderson, 2000). Using calcite, the transformation of lithogenic carbonate which occurs within the soil can be represented by the following reversible equation:



The dissolution of calcite in soils is enhanced by increased levels of CO₂ in the soil and temperature (Van Breemen and Protz, 1988) especially in the root zone of plants where CO₂ levels are over 100 times that of the atmosphere (Suarez, 2000). Percolating water helps in

moving the dissolved calcite to deeper parts of the soil profile as represented by the right side of the above equation. This reduces inorganic C in the soil but also helps in removing CO₂ from the atmosphere. On the other hand, if soil water and the partial pressure of CO₂ in soil air decrease, calcite loses its solubility and consequently precipitates as shown by the left side of Eq. 2. This precipitation results in the formation of pedogenic or secondary carbonates. Generally, pedogenic carbonate formation occurs at a slow rate and ranges from 2 to 10 kg C ha⁻¹ yr⁻¹ (Machette, 1985; Schlesinger, 1985). In Saskatchewan soils, the rate of pedogenic carbonate formation is estimated to range from 9.9 to 13.4 kg C ha⁻¹ yr⁻¹ (Landi, 2002; Landi et al., 2003b; Mermut and Landi, 2004).

In the Canadian System of Soil Classification, the suffix *k* is used to represent carbonate of lithogenic origin as in Bmk and Ck horizons, while the suffix *ca* is used for carbonate of pedogenic origin as in Cca horizon. Using ¹³C, Landi et al. (2003b) showed that the greatest percentage of carbonates is of pedogenic origin in Cca horizons. According to Landi et al. (2003b) the amount of calcium in the soil largely determines the formation of pedogenic carbonate, hence soils containing large amounts of primary carbonates, will on weathering release more Ca for pedogenic carbonate formation in Cca horizons. Other studies in the prairies also have shown that clay-sized calcite dominates pedogenic carbonate (Wang and Anderson, 2000).

The C sequestration ability of these soils is not the only subject of interest. The main activity characteristic of the Prairies is agriculture which has to be supported by highly productive soils. In this case, SOM plays a key role in maintaining soil fertility and other soil properties that are important in ensuring high soil productivity and sustainable agricultural development (Hassink et al., 1997; William et al., 2005). This, therefore, makes C mineralization processes essential in SOM decomposition and the release of nutrients for the maintenance of soil productivity.

Soil organic matter can be divided into two pools: light and heavy fractions (Barrios et al., 1996). The light fraction comprises partially decomposed remains of plants and animals while the heavy fraction is well decomposed with a slow turnover rate and is closely linked with

soil minerals. The light fraction has higher concentrations of C and N than the heavy fraction (Gregorich et al., 1996), with estimated levels of C and N in the light fraction being about 50% and 40%, respectively (Christensen, 1992). Hence it is not surprising that the amount of C mineralized from the light fraction was found to be 2 to 11 times more than that in the heavy fraction (Dalal and Mayer, 1986). The light fraction can also serve as an index of transformations in labile SOM as influenced by land use change and management and other environmental factors that influence microbial activity (Tan et al., 2007) while the heavy fraction can serve as a sink for the storage of soil C (Barrios et al., 1996). Alvarez and Alvarez (2000) examined SOM pools and their relationships with C mineralization and found that biomass C has a positive and strong correlation with total C and the C in the light fraction while Hassink (1995) and Barrios et al. (1996) found that it has a strong correlation with N mineralization rate. The relationship, however, is not strong with the heavy fraction (Alvarez and Alvarez, 2000) because of its low mineralizable C content (Barrios et al., 1996; Whalen et al., 2000). Apart from plant and animal residues, the light fraction has microbial remains with very high turnover rates (Spycher et al., 1983) thus making the correlation between it and C mineralization positive and strong (Alvarez and Alvarez, 2000).

2.2.2.2 Assessing soil C availability

The amount of C available in the soil is an indication of the functional status of the ecosystem. This information can be obtained by measuring the capacity of the soil to transform OC into IC (primarily CO₂). Carbon mineralization is determined by monitoring the evolution of CO₂ from soil samples that are wetted and incubated over a period of time (Haney et al., 2004). Both field and laboratory methods can be used to achieve this. For the purposes of this discussion, only commonly used laboratory methods will be described.

Laboratory methods of assessing C availability mainly involve soil incubations. Short-term incubation experiments involve measuring C mineralization from a few days to a few weeks, and determining mineralization rates. This method gives an indication of the overall bioactivity in the soil under controlled experimental conditions (Hopkins, 2008). The amount of CO₂ produced when mineralization ceases as a result of the depletion of the available SOM

serves as an index of the light fraction pool, which is the form that can be easily mineralized or is readily available to the soil microorganisms (Janzen et al., 1992; Curtin and Wen, 1999; Robertson et al., 1999). Long-term incubation experiments may take several weeks or months. This gives information on both pools of SOM (light and heavy fraction) and allows for the determination of the amount of C mineralized from each pool (Robertson et al., 1999).

Typically, incubation methods involve trapping and measuring CO₂ produced in a closed chamber with an alkali trap or directly sampling CO₂ in the headspace of the closed chamber. With the alkali trap, CO₂ evolved is measured by titrating with a dilute acid (Hopkins et al., 1988; Schinner et al., 1996) whereas the headspace CO₂ is measured using gas chromatography (GC).

In a short-term incubation study to examine the effect of soil properties on SOM mineralization, Riffaldi et al. (1996) found that the rate of mineralization was greater in soils with low C:N ratios. Similar findings were reported by several other researchers (Mellilo et al., 1982; Levi-Minzi et al., 1990; Riffaldi et al., 1996; Nourbakhsh, 2006) where higher C:N ratios have been found to result in slow decomposition rates, largely due to N limitations.

2.2.3 Nitrogen mineralization

The bulk of soil N is in organic form which has to be transformed or mineralized and made available for both plant and microbes to use. In the mineralization process, complex forms of organic N are first depolymerized to small organic N monomers and then subsequently transformed into inorganic form as NH₄⁺ (Schimel and Bennett, 2004; Nasholm et al., 2009). The depolymerization process is crucial to the release of organic N monomers such as amino acids and short peptides which are also available for both microbial and plant use (Schimel and Bennett, 2004). With good oxygen supply, NH₄⁺ is then oxidized to NO₃⁻ by nitrifying bacteria. Nitrogen mineralization involves mainly decomposition of organic residues (plant and animal residues), synthesis of microbial tissue and the eventual production of NH₄⁺. According to the classical view on N-cycling, during the early stages of decomposition there is competition among the microorganisms for N. When microbial demands for N are higher than what is

available in the residue, the microbes make use of what is in the soil solution thus lowering N levels in the soil for some period. The period of N shortage in the soil associated with microbial assimilation is referred as immobilization, and occurs when low quality residue with wide C:N ratio is added to the soil. When microbial demands are satisfied, the C:N ratio narrows and N in excess of microbial demands is released as mineral N or NH_4^+ . Mineralization and immobilization occur together. However, recent advances in our understanding of N-cycling processes suggest that mineralization-immobilization turnover does not always occur in the soil because both plants and microbes can compete for organic N, effectively short-circuiting the mineral N pool (Figure 2.1) (Nannipieri and Eldor, 2009). However, microbial uptake of organic N is followed by intracellular deamination, and ultimately by excretion of excess NH_4^+ .

Generally, substrates with C:N ratios < 20 or N contents $> 1.5\%$ cause net N mineralization to occur while those with ratios higher than 30:1 or N content $< 1.5\%$ promote immobilization of soil inorganic N (Tisdale et al., 1993; Stevenson and Cole, 1999a). The annual turnover of organic N to mineral N is reported to be between 1.5 to 3.5% (Brady and Weil, 2008). This forms a labile N pool which can support plant growth but varies among soil types. Though there are other sources of N supply to the soil, such as N fixation by legumes, fertilizer and manure addition, soils often constitute the primary sources of available N to plants (Campbell et al., 1995).

It is therefore essential to estimate a soil's N supplying capacity so as to make useful decisions concerning fertilizer application and other land management practices. The estimation can be done using N mineralization experiments which make use of a number of N availability indices.

2.2.3.1 Assessing N availability

Availability of N in the soil is assessed using a number of parameters termed soil nitrogen availability indices (SNAIs), which are either biological or chemical (Keeney, 1982). The biological indices commonly used are cumulative N released during two weeks of incubation and potentially mineralizable N, which usually involves several weeks of incubation

and leaching under aerobic or anaerobic conditions (Campbell et al., 1993). The chemical indices involve the selective extraction of a particular form of N in the soil (Curtin and Campbell, 2008).

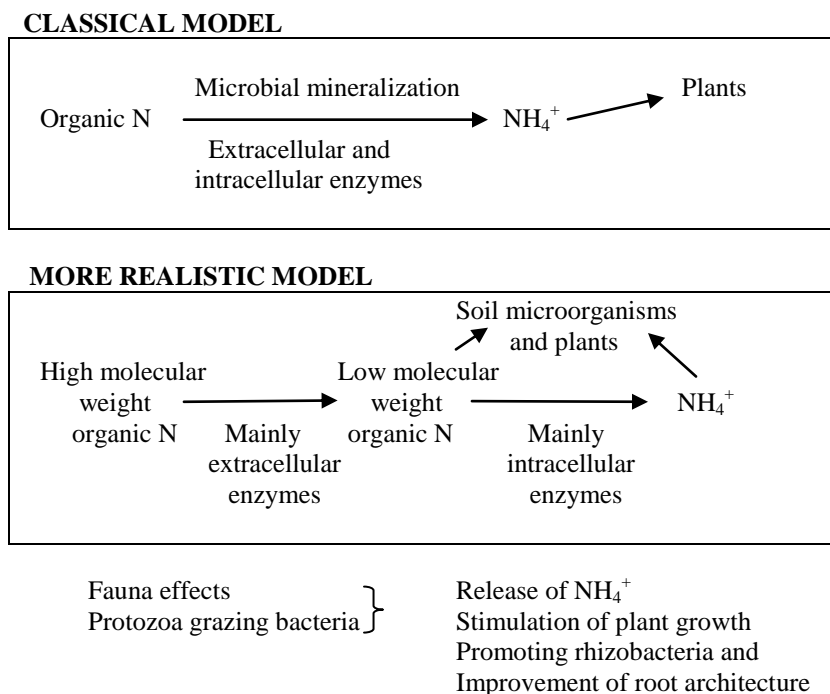


Figure 2.1 Classical versus more realistic models concerning N mineralization

(Adapted from Nannipieri and Eldor, 2009)

Ion exchange membranes are used to extract NO_3^- and NH_4^+ to either assess the native N in the soil or determine the soil N supplying potential (Qian and Schoenau, 1995). Hot 2M KCl is another chemical method used to extract N through the hydrolysis of organic N to NH_4^+ (Gianello and Bremner, 1986). For the purposes of this discussion, only two commonly used biological indices for available N assessment in the soil will be described. These are nutrient supply rate (NSR) using ion exchange membranes and N mineralization potential using a leaching–aerobic incubation technique.

Nutrient supply rate (NSR)

The nutrient supply rate (NSR) is an index for measuring the amount of nutrient adsorbed onto the surface of an ion exchange membrane (IEM) per unit surface area of membrane over the time of burial of the membrane in the soil (Qian et al., 2008). Ion exchange membranes are widely used to determine the amount of nutrient available for plant use (Qian and Schoenau, 2002). They are very easy to use and can reliably measure nutrient availability in a wide range of soils (Saggar et al., 1990; Qian and Schoenau, 2002). On the basis of ionic groups used to prepare the matrix of the membrane, cation exchange membrane (CEM) and anion exchange membrane (AEM) are the main types of IEMs. The CEMs have negatively charged ionic groups on the membrane which preferentially adsorb positive ions. Similarly, the AEMs have positive ionic groups on the membrane and these allow only negative ions to be adsorbed onto the membrane (Xu, 2005; Qian et al., 2008). This preferential transport mechanism is referred to as the Donnan membrane effect or Donnan principle, which is simply the inability of some ions to diffuse out from one region into another system (Sarkar and SenGupta, 2010).

A form of IEM called the Plant Root Simulator (PRSTM) probe was developed by Western Ag Innovations Inc., a research company in Saskatoon, SK, Canada. They are given this trade mark name because they simulate the function of roots by exchanging and adsorbing nutrient ions in the soil solution. These PRSTM probes (both CEM and AEM) have facilitated the assessment of the NSR of soils. They are very useful sinks for the assessment of N mineralized from SOM. According to Qian and Schoenau (1997) the amount of nutrient adsorbed onto the membrane is a function of time and surface area of the membrane. A longer residence time in the soil results in more nutrient adsorption onto the membrane. Though there seems to be no agreement on the duration of burial among researchers, Qian and Schoenau (1995) consider a 2 wk burial adequate, while others (Drohan et al., 2005) recommend burial of the probes for a month.

Potentially mineralizable N (N_o)

Stanford and Smith (1972) introduced the concept of potentially mineralizable N (N_o) by pioneering long-term studies to determine the N supplying power of soils with varying physico-chemical properties. The N_o is that fraction of the organic N pool that is subject to

mineralization, assuming the process follows first order kinetics (Smith et al., 1980). Over a 30 wk incubation period with periodic leaching, Stanford and Smith (1972) found that the mineralization rate was constant for most soils and that a linear relationship existed between cumulative N mineralization and the square root of the time of incubation. In order to estimate N_o , they used a first-order kinetic model, with the assumption that N mineralization rate is proportional to the mineralizable pool of N_o according the relation $dN/dt = -k_N N$ (Stevenson, 1965).

In the form of a single exponential model, the equation becomes:

$$N_t = N_o (1 - e^{-k_N t}) \quad [\text{Eq. 3}]$$

where N_t is N mineralized at time t ,

N_o is potentially mineralizable N and

k_N is the N mineralization rate constant.

In fitting the curve to estimate N_o , Stanford and Smith (1972) obtained a better fit for data from 3 to 30 wk of incubation. There was an initial mineralization flush in the first two weeks of incubation, which was attributed to soil pretreatment. However, the following concerns have been expressed by many investigators:

- values of the mineralization constant, k_N , show wide variation among different soils (Juma et al., 1984; Curtin and Wen, 1999);
- an increase in incubation period results in high N_o values and a corresponding decrease in k_N values (Dou et al., 1996), thus implying that the mineralizable pool of N is not fixed in the soil (Wang et al., 2003);
- procedures and conditions for incubation are variable for the numerous studies carried to determine N_o and k_N , thus making it difficult to compare findings (Wang et al., 2003). In some studies, incubation temperature ranged from 20 °C (Christensen and Olesen, 1998) to 40 °C (Campbell et al., 1981) while incubation period ranged from less than 12 wk (Bronson et al., 2001) to 60 wk (Dendooven et al., 1997).

Alternative models, like the double exponential model, have been proposed to account for the initial flush in mineralization during the first two weeks of incubation (Jones, 1984; Beauchamp et al., 1986) and also the initial lag observed during N mineralization (Ellert and Bettany, 1988). However, it was found that the pool sizes determined in these models varied with time and also resulted in higher values than the amount of organic N present in the soil (Wang et al., 2003). To overcome these problems when using the first order kinetic model to determine N_o , Wang et al. (2003) suggested that temperature and moisture should be maintained at 35 °C and 55 % to 65% moisture holding capacity (or -30 to -10kPa) respectively with a mineralization rate constant at 0.054 wk^{-1} .

Over the years, soil NO_3^- -N level has been used as a basis for N fertilizer recommendations worldwide. However, soil NO_3^- -N is not a surrogate for N supplying power of soils for plant uptake. Besides, the nitrate concentration in soils varies with time and ambient conditions at sampling. The potentially mineralizable N_o has been found to be a more realistic index for assessing N availability in soils (Palm et al., 1993; Hole et al., 2005) because of its strong relationship with the labile pool of SOM and microbial activity (Robertson et al., 1999; El-Ghamry et al., 2001). Knowledge of N_o can be very beneficial in estimating N mineralization and also making better soil fertility assessment and fertilizer recommendations (Campbell et al., 1995; Robertson et al., 1999; Schomberg et al., 2009). Sharifi et al. (2007) evaluated a wide range of topsoils taken from different climatic zones across Canada and the United States for their N_o levels using the aerobic incubation procedure of Campbell et al. (1993). They observed three pools of mineralizable N. The first pool is N mineralized in the first-two weeks of incubation, representing the initial mineralization flush observed by Stanford and Smith (1972). This pool had a mean N level of 21 mg kg^{-1} representing 1.3% total organic N. The second pool represents N mineralized in 22 weeks after the first-two weeks of incubation. This has a mean N level of 75 mg kg^{-1} or 4.4% of total organic N. The third pool represents N_o that was obtained by using the first order kinetic model. Sharifi et al. (2007) found this pool to have a mean N value of 26 mg kg^{-1} (or 1.3% of total organic N).

The above range of N_o values are consistent with what has been found by Jalil et al. (1996) and Curtin and Wen (1999) for some Saskatchewan soils. The values, however, are below the levels reported by Walley et al. (2002), also for Saskatchewan soils. Two main factors responsible for the observed differences in N_o levels are low incubation temperatures (25 °C instead of 35 °C) and soils with low SOC and clay contents (Sharifi et al., 2007). Generally, N mineralization shows more positive responses to temperature increases than moisture (Zak et al., 1999; Wang et al., 2003).

3.0 C AND N MINERALIZATION IN WETLAND SOILS OF THE CANADIAN PRAIRIES

3.1 Introduction

Wetlands form an integral part of the agricultural landscapes of the Canadian Prairies. For example, Hogan and Conly (2002) recorded 216 wetlands spread over an area of 3.84 km² within the St. Denis National Wildlife Area in Saskatchewan, most of which have been converted to annual crop production. The wetlands within the agricultural fields contain a wide range of soils with distinct morphological and chemical properties, and are classified into different taxa of the Canadian System of Soil Classification. An implicit assumption of soil classification is that the genetic differences used in the classification also correspond to functional differences among the soil classes in a range of soil processes, but this assumption has rarely been tested for wetland soils of western Canada. The main goal of this thesis is to determine if there are differences in C- and N-cycling processes associated with different wetland soil classes in a typical Canadian prairie wetland site.

The occurrence of a range of wetland soils in close proximity to each other at the research site can be attributed to prevailing hydrology and soil-landscape relationships. Studies have shown that movement of water to the water table (termed recharge), lateral flow (or flowthrough) within the soil, and water flow towards the soil surface (termed discharge) are the main hydrological pathways that determine which soils develop within these wetlands (Miller et al., 1985; Richardson et al., 1992). At sites of recharge, which are mainly the depressions, the soils are leached of solutes such as carbonates, sulphates and chlorides as water infiltrates through them. This results in the development of carbonate-free and non-saline soils with deep sola and characteristic gley features as seen in the Aeg and Btg horizons of Humic Luvic Gleysols (HLG) (Miller et al., 1985). Wetlands that have smaller catchment areas and hence shorter periods of inundation typically have Chernozemic soils of the Eluviated subgroup. They differ from the HLG by being better drained and also experience lateral flow conditions leading to the formation of Ae horizons and Btj or Bt horizons.

At discharge sites, which occur in a fringe around the wetlands, capillary rise causes water to flow towards the dry soil surface where evaporation leads to the deposition of solutes such as calcium carbonate in the soil (Miller et al., 1985; Richardson et al., 1992). The soil is thus enriched in carbonates and other solutes and recognized by the presence of Bmk and/or Cca horizons typical of a Calcareous Dark Brown Chernozem (CDBC). Given the observed genetic and morphological differences in these three wetland soils, it is not known whether they also differ in terms of their C and N mineralization.

Since all the three soils identified in this study are been cultivated, issues such as low organic C levels, together with declining soil fertility such as low N levels can arise, and this can be linked with reduced OM levels in the soils. The loss of SOC under cultivation has been observed in several studies (Landi et al., 2004), and it follows that nutrients such as N, that are tightly linked to organic C-cycling, share similar losses. Consequently, to evaluate the potential productivity of wetland soils, it will be very useful to have an improved knowledge of the mineralization rate and potential of the SOC and SON reserves. This information can be used to provide adequate SOC levels, together with associated nutrients in the soils for sustainable land use and management.

Interest in assessing the C and N mineralization potential of the above wetland soils, which are now in agricultural production within a hummocky landscape of the Canadian prairies, led to the objectives of this study, which were:

1. To compare C and N mineralization parameters/attributes in horizons of the three wetland soil classes;
2. To evaluate the relationships between soil factors and C and N mineralization in the three wetland soil classes.

3.2 Materials and methods

3.2.1 Study site

The study site is located in the St. Denis National Wildlife Area (SDNWA), 52° 12' N latitude, 106° 5' W longitude and 40 km east of Saskatoon, Saskatchewan. The SDNWA is in the Dark Brown soil zone of Saskatchewan, with soils developed from moderately fine to fine textured, moderately calcareous, loamy glacio-lacustrine deposits and unsorted glacial till. The area is characterized by hummocky landscape with slopes ranging from 10 to 15% (Miller et al., 1985).

3.2.2 Land use history

The original vegetation in the area was predominantly grassland with aspen groves. The main grass species are spear grass (*Stipa spartea* var. *curtiseta*), wheat grass (*Agropyron dasystachyam*) and fescue (*Festuca scabrella*) (Miller, 1983). By 1950, cultivated land (> 50%), native grassland (> 20%) and wetlands (10%, which covers approximately 40 ha) were the main land uses in the area prior to the establishment of the SDNWA (Van den Bos, 2005). Following the establishment of the SDNWA in the late 1960s, cultivated land area dwindled to about 40% by the late 1990s, due to conversion of portions into permanent grass cover with the objectives of reducing tillage erosion and providing adequate nesting grounds for wildlife (van der Kamp et al., 2003). Though cultivated land area has reduced it is still the main land use in the area (including the area in which the study area falls) with canola and wheat as the main crops.

3.2.3 Research design and soil sampling strategy

Wetlands were selected on the basis of previous studies by Bedard-Haughn and Pennock (2002). Four representatives of each of the three soil classes were selected after an initial soil reconnaissance using a Dutch auger. The selected soils were Calcareous Dark Brown Chernozem (CDBC), Eluviated Dark Brown Chernozem (EDBC), and Humic Luvic Gleysol (HLG). Soil cores were taken by means of a truck-mounted hydraulic corer, equipped with a 6.2 cm inner diameter core.

Individual sample cores (108) were separated on the basis of pedological horizons, not fixed sampling depth. For each soil, three horizons were sampled within an average depth range of 70 cm. Subsamples were collected from the uppermost 15 cm of each horizon (Figure 3.1).

3.2.4 Incubation studies

3.2.4.1 Sample preparation and nitrogen supply rate (NSR) determination

Soil samples collected for the mineralization studies were prepared and stored as recommended by Campbell et al. (1993). From the field, the samples were refrigerated immediately at 4 °C. They were later air-dried and stored at 4 °C prior to incubation.

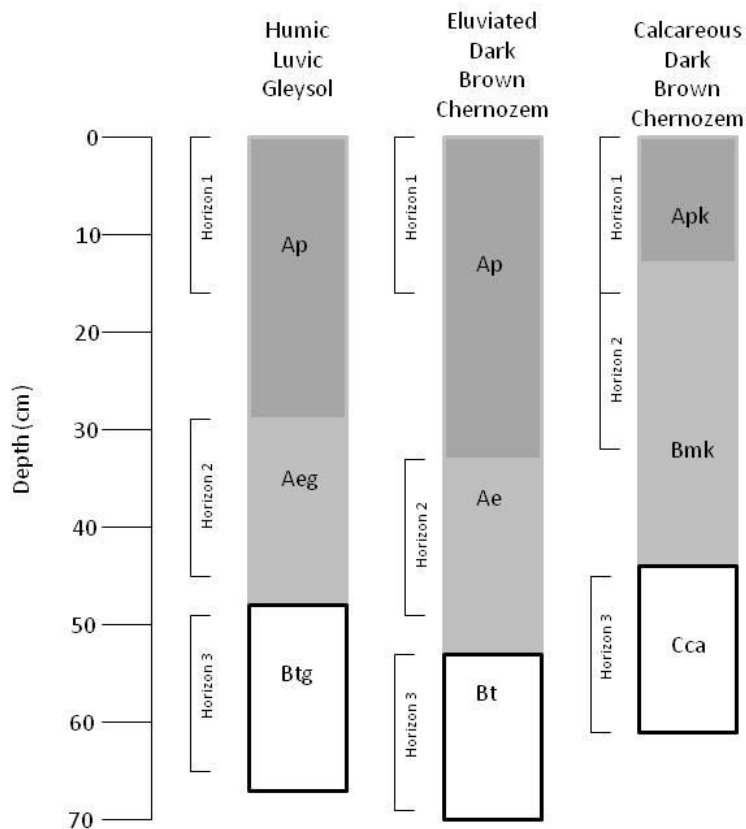


Figure 3.1 Mean horizon thickness for three soil classes and mean position of 15-cm sampling increments for horizon-based sampling.

The NSR was determined by incubating cation and anion exchange membranes in moistened soil according to Qian et al. (2008). Briefly, plant root simulator (PRSTM) probes were inserted into 150 g of each soil, previously packed to approximately equal volumes in 40 dram vials, and moistened to field capacity with distilled water. Prior to insertion, the PRSTM probes (both cation and anion exchange membranes) were washed and charged. Specifically, the cation exchange membranes initially were soaked in distilled water overnight and later immersed in 0.5M HCl to charge the exchange sites with H⁺, while the anion exchange membranes were immersed in 0.5M NaHCO₃ to charge them with HCO₃⁻ ions (Qian et al., 2008). Sample and control vials (i.e., no soil) were then placed in 1 L Mason jars fixed with rubber septa to allow for headspace sampling of CO₂ evolved. The vials were prepared in duplicates. Each jar was closed and then incubated in the dark under laboratory conditions (22 °C) for 16 d.

By means of a syringe, 20 mL of the headspace was sampled every 2 d and transferred to 12 mL preevacuated Exetainer vials (Labco, UK). After each sampling, the jars were opened for 2 h to replenish the atmosphere before continuing with the incubation (De Neve and Hofman, 2000). Carbon dioxide concentrations of the headspace samples were determined using a Varian Model CP 4900 Micro-GC equipped with a micro-TCD and Poraplot U column (injector temperature = 110 °C, column and detector temperature = 50 °C). Ultra-high purity (UHP) helium was used as the carrier gas.

After two weeks of incubation in the Mason jars, the PRSTM probes (cation and anion) were removed from the soil and washed free of soil particles using distilled, deionized water. The ions, specifically nitrate (NO₃⁻) and ammonium (NH₄⁺), captured on the membranes were eluted with 0.5M HCl and their concentrations determined on an Auto Analyzer (Qian and Schoenau, 1995). According to Qian and Schoenau (1995, 2002) the amount of mineral N produced within two weeks of incubation correlates very well with N uptake by plants and also gives an indication of the N supplying potential of the soil.

3.2.3.2 Determination of nitrogen mineralization potential (N_o)

An aerobic incubation technique was used to determine N mineralization potential (N_o) of the soils using the method described by Campbell et al. (1993). The incubation procedure and extraction apparatus was that described and used by Yates (2001). For each sample, 100 g oven-dry equivalent of pre-sieved field moist soil were mixed with 100 g of acid-washed quartz sand to give a 1:1 soil-sand mixture. Each mixture was placed in an incubation tube and then covered with a 5-cm layer of plastic beads to forestall soil dispersion during addition of CaCl_2 solution and also to reduce moisture loss. To each sample, 200 mL of 0.01M CaCl_2 were applied in 20 mL aliquots to leach native mineral N before incubation. Moisture content of the samples was reduced to 20% by weight using a bench top vacuum to facilitate the addition of 10 mL of a minus N nutrient solution comprising 0.002M CaSO_4 , 0.002M MgSO_4 , 0.005M $\text{Ca}(\text{H}_2\text{PO}_4)_2$, and 0.0025M K_2SO_4 . Following this, deionized water was added to bring the moisture content to 22.5%.

The incubation tubes were placed in 76 L plastic containers in a growth chamber at a temperature of 35 °C. This is the optimum temperature needed to obtain maximum mineralization (Wang et al., 2003). In order to maintain high and constant relative humidity and also reduce moisture loss from the samples, large containers with water were kept in the growth chamber. The moisture status of the samples was monitored weekly and deionized water added to maintain 22.5% moisture on w/w basis. During incubation, each sample was leached every two weeks for 12 weeks and then once after an additional four weeks to give a total incubation period of 16 weeks. Leachates were filtered through Whatman No. 4 filter paper and then analyzed for NO_3^- -N and NH_4^+ -N using a Technicon Auto Analyzer II System.

3.2.4 Laboratory methods

Particle size distribution of the soils was determined using a Horiba LA950 Laser Scattering Particle Size Analyzer (Horiba Instruments Inc.). Prior to determination of particle size approximately 0.5 to 1.0 g of each soil was weighed into a 50 mL Falcon tube and pretreated with 10 mL of 30% H_2O_2 to remove OM (Kroetsch and Wang, 2008). When frothing ceased, 10 mL of 50 g L^{-1} sodium hexametaphosphate (calgon) were added to facilitate dispersion of the

soil particles (Eshel et al., 2004). The falcon tubes were closed and the soil mixture was shaken overnight on a reciprocating shaker to ensure adequate dispersion of the soils. Soil pH was measured by means of an Accumet pH meter AP85 (Fisher Scientific) with a soil:water ratio of 1:2 as described by Hendershot et al. (2008a). Organic C was determined by dry combustion using the LECO CR-12 carbon analyzer at a temperature of 840 °C; total C and total N were determined by dry combustion using a LECO CNS-2000 analyzer set a temperature of 1350 °C. Inorganic C was determined as the difference between total C and organic C. Carbon and N ratios also were calculated for each soil.

3.2.5 Data analyses

An exploratory data analysis was performed to determine the nature of the distribution for each soil variable and C and N mineralization. Data distribution was tested for normality using the Shapiro-Wilk test at an alpha value of 0.05. Not all variables approximated a normal distribution after the test. In order to achieve uniformity, data were log-transformed after which parametric statistics were used for analysis. One-way analyses of variance were used to determine whether there were any differences in C and N mineralization, and properties of the soils. Differences among means were tested using Tukey's HSD test at a 0.05 alpha value.

A first-order model was used to determine C mineralization parameters. The following equation (Murwira et al., 1990) was used:

$$C_t = C_o (1 - e^{-k_C t}) \quad [\text{Eq. 4}]$$

where

C_t = measured cumulative C mineralized in time t (mg CO₂-C kg⁻¹soil);

C_o = potential C mineralization (mg CO₂-C kg⁻¹soil);

k_C = C mineralization rate constant (mg CO₂-C kg⁻¹soil d⁻¹) and t is the time for mineralization (days).

Non-linear least square regression was performed through curve fitting using solver add-in of Microsoft Excel (Version 2007) as described by John (1998). The model was fitted to the experimental data to determine the values of C_o and k_c . The non-linear least square regression is based on first-order kinetics (Campbell et al., 1993). A correlation analysis was performed using Pearson's correlation matrix to determine relationships between C mineralization parameters [i.e. C mineralization rate (rC_{min}), C_o , k_c and $C_o k_c$], and each of the following characteristics: sand, silt, clay, pH, OC, IC, total N and C:N ratio. The correlation was performed with data grouped on basis of horizons and also to establish soil-specific relationships. The parameter $C_o k_c$ was included because many researchers consider it to be an index that provides a better assessment of the OM quality and degree of microbial degradation of residue than the individual parameters (Murwira et al., 1990; Saviozzi et al., 1993; Pascual et al., 1998; Nourbakhsh, 2006). The potentially mineralizable N and mineralization rate constant were also obtained using the first-order model, according to Campbell et al. (1993):

$$N_t = N_o (1 - e^{-k_N t}) \quad [\text{Eq. 5}]$$

where

N_t = cumulative N that is mineralized in time t (mg N kg⁻¹soil);

N_o = potentially mineralizable N (mg N kg⁻¹soil);

k_N = N mineralization rate constant (mg N kg⁻¹soil wk⁻¹)

The parameters N_o and k_N were estimated through similar steps as in the case of C_o and k_c .

The relationship between N mineralization parameters [N mineralization rate (rN_{min}), N_o , k_N and $N_o k_N$] and the soil properties were determined as in the case of C mineralization. The $N_o k_N$ parameter was included for the reasons similar to those stated for $C_o k_c$. All analyses, apart from the model parameters, were performed in SPSS (SPSS version 16.0, SPSS Inc., USA).

3.2.6 Calculations

CO₂ data from GC

Data from the GC were initially in ppmv ($\mu\text{L CO}_2 \mu\text{L}^{-1} \text{air}$) and these were converted to $\text{mg CO}_2\text{-C kg}^{-1} \text{soil}$ as follows:

$$1 \text{ ppmv} = \left(\frac{\mu\text{L CO}_2}{\text{L air}} \right) \left(\frac{1 \mu\text{mol CO}_2}{22.4 \mu\text{L CO}_2} \right) \left(\frac{44.01 \mu\text{g CO}_2}{\mu\text{mol CO}_2} \right) \left(\frac{\text{headspace volume (L)}}{150 \text{ g soil}} \right) = 13.1 \times 10^3 \mu\text{g CO}_2 \text{ g}^{-1} \text{soil} \quad [\text{Eq.6}]$$

Expressing Eq. 6 in terms of $\text{mg CO}_2\text{-C kg}^{-1} \text{soil}$ becomes :

$$13.1 \times 10^3 \mu\text{g CO}_2 \text{ g}^{-1} \text{soil} = (13.1 \text{ mg} \times 10^3 \text{ CO}_2 \text{ kg}^{-1} \text{soil}) \left(\frac{12.01 \text{ mg CO}_2\text{-C}}{44.01 \text{ mg CO}_2} \right) = 3.57 \times 10^3 \text{ mg CO}_2\text{-C kg}^{-1} \text{soil} \quad [\text{Eq.7}]$$

where: $22.4 \mu\text{L CO}_2$ = (micro)molar volume of gas at STP; $44.01 \mu\text{g}/\mu\text{mol CO}_2$ = molecular weight of CO_2 ; 150 g soil = weight of soil in vial ; $12.01 \text{ mg CO}_2\text{-C}$ = atomic weight of C.

Other C mineralization calculations:

- (i) Total C mineralization (ΣC_{\min}) was obtained by summing the individual values for each sampling time;
- (ii) C mineralization rate was obtained by dividing ΣC_{\min} by the duration of the incubation experiment (i.e. 16 d);
- (iii) C mineralization parameters (ΣC_{\min} , C_0 and C_0k_C) were normalized with respect to total OC by the dividing each parameter by the OC content of the soil.

Nutrient supply rate (NSR)

The NSR using PRSTM probes was determined using a modified version of the equation of Qian et al. (2008):

$$\text{NSR } (\mu\text{g cm}^{-2} \text{wk}^{-1}) = (\text{C} * \text{V})/\text{ST} \quad [\text{Eq. 8}]$$

where

C = concentration of adsorbed ion (cation or anion in $\mu\text{g mL}^{-1}$);

V = volume of eluent (mL)

S = surface area of PRSTM probe (16.5 cm^2).

T = duration of incubation (14 d). T was introduced in the original equation of Qian et al. (2008) in order to calculate the rate of nutrient supply.

N mineralization

Calculations for total N mineralization (ΣN_{\min}) and rN_{\min} were similar to those for determining the C mineralization parameters above. To obtain rN_{\min} , ΣN_{\min} was divided by 16 wk. Data for the first two weeks of N mineralization were not used in the curve fitting procedure to estimate N_0 because this represents the initial lag of mineralization (Stanford and Smith, 1972). Nitrogen mineralization parameters (ΣN_{\min} , N_0 and $N_0 k_N$) were normalized with respect to total N in the soil.

N data from Auto Analyzer (AA)

Data from the AA were in ppm. These were converted to mg kg^{-1} soil as described below:

$$\text{ppm N} = \text{mg N L}^{-1} \quad [\text{Eq. 9}]$$

Considering the volume of extractant used, the total amount of N extracted will be:

$$\text{Total N extracted (mg N)} = \text{mg N L}^{-1} \times 0.2 \text{ L} \quad [\text{Eq. 10}]$$

Taking mass of soil into consideration, Eq. 10 becomes:

$$\text{Total N (mg N kg}^{-1}\text{)} = [(\text{mg N L}^{-1} \times 0.2 \text{ L}) / 0.2 \text{ kg soil}] \quad [\text{Eq. 11}]$$

3.3 Results

3.3.1 Soil properties

Horizon thickness varied among soils (Table 3.1) with the EDBC soils exhibiting the greatest mean horizon thickness for the surface horizon and the CDBC soils the lowest (Table 3.1). The HLG had the lowest mean horizon thickness for the middle horizon while the highest was found in the CDBC soils.

Particle size distribution showed that irrespective of soil type, coarse textures (i.e. sandy loams) were dominant in the surface layers. Within each soil profile, clay content increased with depth. Sand values in the surface were greater than 50% in all the soils (Table 3.1) but no significant differences were observed among the surface or lower horizons.

Table 3.1 Particle size distribution in horizons of selected wetland soils.

| Soil type† | Horizon | Thickness | Sand | Silt | Clay |
|------------|------------------|------------|------------|-----------|------------|
| | | cm | | % | |
| | <i>Horizon 1</i> | | | | |
| HLG | Ap | 29.7 (12)‡ | 55.9 (7)a§ | 33.6 (7)a | 10.5 (3)ab |
| EDBC | Ap | 33.6 (14) | 58.8 (3)a | 34.7 (3)a | 6.5 (1)b |
| CDBC | Apk | 13.8 (6) | 52.7 (7)a | 33.1 (3)a | 14.2 (5)a |
| | <i>Horizon 2</i> | | | | |
| HLG | Aeg | 18.3 (3) | 40.9 (3)a | 42.0 (3)a | 17.0 (1)b |
| EDBC | Ae | 21.2 (6) | 50.1 (11)a | 30.1 (3)b | 19.8 (9)b |
| CDBC | Bmk | 38.4 (4) | 36.2 (14)a | 27.0 (5)b | 36.9 (12)a |
| | <i>Horizon 3</i> | | | | |
| HLG | Btg | 46.4 (5) | 31.2 (8)a | 31.7 (1)a | 37.2 (8)a |
| EDBC | Bt | 35.7 (2) | 39.3 (15)a | 27.3 (5)a | 33.4 (11)a |
| CDBC | Cca | 55.3 (1) | 34.1 (7)a | 26.3 (2)a | 39.6 (8)a |

† HLG: Humic Luvisol; EDBC: Eluviated Dark Brown Chernozem; CDBC: Calcareous Dark Brown Chernozem

‡ Columns have mean values for properties with standard deviation in parentheses

§ Mean values followed by the same letter within a column for a given horizon are not significantly different according to Tukey's test ($P < 0.05$)

Sand content decreased with depth in all the soils (Table 3.1). Silt content of the second horizon in the HLG was significantly greater than those of EDBC and CDBC soils but no differences were observed for the other horizons. The third horizons of all three soils had medium textures (clay loam). The highest clay content was found in the Cca horizon of the CDBC soils and the lowest in the Bt horizon of the EDBC soils (Table 3.1).

The soils were generally alkaline and there was little variation in pH in the surface, second and third horizons of the HLG and EDBC (Table 3.2). However, pH values in the CDBC were significantly greater than those observed for the HLG and EDBC soils. The higher pH values in the CDBC could be attributed to the presence of carbonates in these soils. In the field these soils showed moderate to strong effervescence while no effervescence was observed in the other soils.

Organic carbon (OC) levels were highest in the surface horizons and decreased with depth in all soil types (Table 3.2). However, within horizons, there were no significant differences in OC among the soil types.

Total N levels followed a pattern similar to OC levels (Table 3.2) with total N decreasing with depth in each soil. The highest levels were found in the surface horizons, with the Ap horizon of the HLG showing the highest values. Overall, the lowest N levels were in the CDBC soils with the lowest value found in the third horizon. In a manner similar to OC and N values, C:N ratios decreased with depth, and in all cases, C:N ratios were less than 10. However, there were no significant differences across each group of horizons among the three soils.

Inorganic carbon (IC) levels in all horizons were generally greatest in the CDBC soils (Table 3.2). This was reflected in the observed high pH levels in these soils. Unlike OC, IC levels increased with depth in the CDBC soils with the highest levels found in the third horizon. In both the HLG and EDBC soils IC levels were below 5 g kg⁻¹ soil in all the three horizons of each soil. There were no significant differences in IC levels among the three surface horizons. However, IC levels in the second and third horizons of CDBC soils were significantly greater than the levels found in similar horizons in the HLG and EDBC soils.

Table 3.2 Distribution of some chemical properties in horizons of three wetland soils.

| Soil type† | Horizon | Thickness cm | pH | Organic carbon | Inorganic carbon | Total nitrogen | C:N ratio¶ |
|------------------|---------|-----------------|-------------|-------------------------|---------------------|-------------------|--------------|
| | | | | g kg ⁻¹ soil | | | |
| <i>Horizon 1</i> | | | | | | | |
| HLG | Ap | 29.7 (12)‡ | 8.1 (0.1)b§ | 27.8 (5.0)a | 4.0 (1.2)a | 3.61 (0.50)a | 7.66 (0.50)a |
| EDBC | Ap | 33.6 (15) | 8.1 (0.1)b | 24.9 (3.8)a | 1.5 (1.5)a | 3.03 (0.50)a | 8.28 (0.79)a |
| CDBC | Apk | 13.8 (6) | 8.3 (0.1)a | 21.8 (4.8)a | 5.1 (3.8)a | 2.79 (0.79)a | 7.97 (0.72)a |
| <i>Horizon 2</i> | | | | | | | |
| HLG | Aeg | 18.3 (3) | 8.0 (0.1)b | 11.8 (6.6)a | 1.3 (0.5)b | 1.70 (0.75)a | 6.73 (0.85)a |
| EDBC | Ae | 21.2 ((6) | 8.1 (0.1)b | 6.3 (4.4)a | 1.3 (0.9)b | 1.05 (0.30)a | 5.42 (2.69)a |
| CDBC | Bmk | 38.4 (4) | 8.6 (0.3)a | 6.5 (2.8)a | 17.3 (2.8)a | 1.05 (0.19)a | 5.80 (1.66)a |
| <i>Horizon 3</i> | | | | | | | |
| HLG | Btg | 46.4 (5) | 8.0 (0.1)b | 5.5 (3.1)a | 2.3 (0.6)b | 1.10 (0.18)a | 4.86 (2.51)a |
| EDBC | Bt | 35.7 (2) | 8.1 (0.2)b | 3.4 (0.6)a | 1.3 (0.7)b | 0.84 (0.09)ab | 4.10 (0.62)a |
| CDBC | Cca | 55.3 (1) | 8.6 (0.3)a | 3.9 (2.0)a | 20.9 (5.3)a | 0.64 (0.25)b | 6.04 (2.89)a |

†HLG: Humic Luvic Gleysol; EDBC: Eluviated Dark Brown Chernozem; CDBC: Calcareous Dark Brown Chernozem

‡Columns have mean values for all the properties with standard deviation in parentheses

§Mean values followed by the same letter within a column for a given horizon are not significantly different according to Tukey's test ($P < 0.05$)

¶C:N ratio: carbon nitrogen ratio

3.3.2 Carbon mineralization

The surface horizons showed the highest cumulative C mineralization which was represented by CO₂ production ($> 150 \text{ mg CO}_2\text{-C kg}^{-1} \text{ soil}$, Figure 3.2, Table 3.3) with the Ap horizon of HLG being higher than Ap of EDBC and Apk of CDBC. Mean cumulative C mineralization in the second and third horizons of the three soils were very similar and ranged from 44 to 77 mg CO₂-C kg⁻¹ soil. The mean C mineralization rate was highest (at 13.4 mg CO₂-C kg⁻¹ d⁻¹) in the first horizon of the HLG and decreased sharply with depth in the lower horizons (Table 3.3). Similar patterns in mean C mineralization rates were observed in the EDBC and CDBC soils (Table 3.3). The lowest rate of C mineralization occurred in the third horizon of the CBDC soils. Mean C mineralization rate followed a pattern similar to cumulative C mineralization.

The differences in C mineralization rate and total C mineralization (shown by CO₂ production) across the three soil classes for a given increment were relatively consistent (Table 3.3). Generally the values were highest (and statistically different) for the HLG soils compared to the CDBC soils, and the EDBC soils occupied an intermediate position.

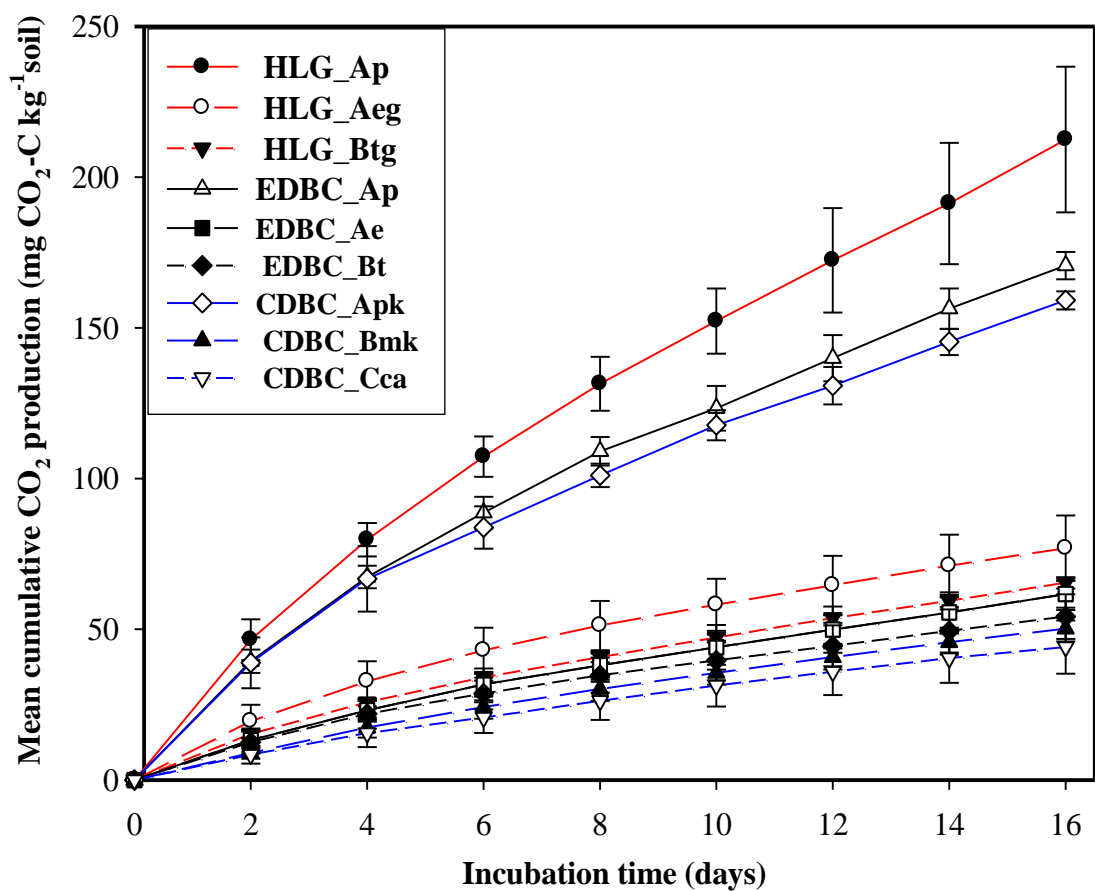


Figure 3.2 Mean cumulative CO₂ production in three wetland soils at SDWNA

HLG: Humic Luvic Gleysol; EDBC: Eluviated Dark Brown Chernozem;

CDBC: Calcareous Dark Brown Chernozem; Error bars are for standard deviation (n=4)

Table 3.3 Total C mineralization (ΣC_{\min}), mean potential C mineralization (C_o), C mineralization rate (rC_{\min}), C mineralization rate constant (k_C) and initial potential mineralization rate ($C_o k_C$).

| Soil type† | Horizon | ΣC_{\min} | C_o | rC_{\min} | k_C | $C_o k_C$ |
|------------|------------------|---|---|---|-----------------|---|
| | | mg CO ₂ -C kg ⁻¹ soil | mg CO ₂ -C kg ⁻¹ soil | mg CO ₂ -C kg ⁻¹ soil d ⁻¹ | d ⁻¹ | mg CO ₂ -C kg ⁻¹ soil d ⁻¹ |
| | <i>Horizon 1</i> | | | | | |
| HLG | Ap | 212.5 (24)a‡ | 322.0 (12)a§ | 13.4 (1.5)a | 0.086 (0.005)a | 26.8 (9.6)a |
| EDBC | Ap | 170.7 (5)b | 230.4 (10)b | 10.9 (0.3)ab | 0.082 (0.011)a | 18.3 (2.2)a |
| CDBC | Apk | 159.1 (3)b | 207.1 (23)b | 8.7 (2.5)b | 0.092 (0.029)a | 18.0 (3.4)a |
| | <i>Horizon 2</i> | | | | | |
| HLG | Aeg | 76.9 (13)a | 94.3 (11)a | 4.8 (0.8)a | 0.102 (0.024)a | 9.3 (2.2)a |
| EDBC | Ae | 61.7 (6)ab | 90.5 (12)a | 3.9 (0.4)ab | 0.073 (0.020)a | 6.4 (1.2)a |
| CDBC | Bmk | 50.2 (4)b | 100.3 (39)a | 3.2 (0.3)b | 0.055 (0.027)a | 4.7 (0.9)a |
| | <i>Horizon 3</i> | | | | | |
| HLG | Btg | 65.4 (2)a | 89.6 (13)a | 4.1 (0.1)a | 0.081 (0.016)a | 7.1 (0.7)a |
| EDBC | Bt | 54.2 (9)ab | 73.0 (16)a | 3.2 (0.4)b | 0.090 (0.031)a | 6.3 (2.3)ab |
| CDBC | Cca | 44.1 (9)b | 88.9 (37)a | 2.8 (0.5)b | 0.054 (0.024)a | 4.1 (1.2)b |

†HLG: Humic Luvic Gleysol; EDBC: Eluviated Dark Brown Chernozem; CDBC: Calcareous Dark Brown Chernozem

‡Columns have mean values for mineralization parameters with standard deviation in parentheses

§Mean values followed by the same letter within a column for a given horizon are not significantly different according to Tukey's test ($P < 0.05$)

The pattern was slightly different for potential C mineralization (C_o). Potential C mineralization for horizon 1 of the HLG was significantly greater ($P < 0.05$, Table 3.3) than the corresponding CDBC soils, although neither differed significantly from the C_o of the EDBC. There was no significant difference in the C_o values for all the second or third horizons of the three soils (Table 3.3).

There were no differences in k_C values irrespective of horizon and soil type. Another useful parameter is the product of C_o and k_C , ($C_o k_C$) which is referred to as the initial potential C mineralization rate. This parameter is considered a better estimator of potential mineralization than when C_o and k_C are treated separately (Riffaldi et al., 1996). Values of $C_o k_C$ for the three groups of horizons were not significantly different ($P < 0.05$, Table 3.3) for the three soils. However, $C_o k_C$ values for the HLG soils were consistently greater than for the CDBC, and the values for the EDBC were intermediate (Table 3.3).

The C mineralization parameters were normalized against OC content for each soil (Table 3.4). This was done by dividing each parameter with the respective OC content. Following normalization, no significant differences were observed between any of the ratios ($\Sigma C_{min}:OC$, $C_o:OC$ and $C_o k_C:OC$) for all horizons, and for all three soils. Values for $\Sigma C_{min}:OC$ ranged from 7 to 8 mg $CO_2-C\ g^{-1}\ C$ in horizon 1, representing 0.7 to 0.8% of soil OC mineralized. Values for horizon 2 ranged from 6 to 10 mg $CO_2-C\ g^{-1}\ C$ (or 0.6 to 1% soil OC). Values for horizon 3 were greatest and ranged from 11 to 16 mg $CO_2-C\ g^{-1}\ C$ (or 1.1 to 1.6% soil OC). Like $\Sigma C_{min}:OC$, $C_o:OC$ ratios showed a general increase with depth (Table 3.4). Values for horizon 1 represent 0.94 to 1.18% of soil OC that potentially could be mineralized; horizon 2 showed a range from 0.97 to 1.67% of OC while for horizon 3, the range was from 1.34 to 2.24% of soil OC that potentially could be mineralized.

Table 3.4 Normalized carbon mineralization parameters with soil organic carbon.

| Soil type† | Horizon | $\Sigma C_{\min}:OC‡$ | $C_o:OC$ | $C_o k_c:OC\#$ |
|------------|------------------|---|--------------|---|
| | | mg CO ₂ -C g ⁻¹ C | | mg CO ₂ -C g ⁻¹ C d ⁻¹ |
| | <i>Horizon 1</i> | | | |
| HLG | Ap | 7.9 (1.3)a§ | 11.8 (4.5)a¶ | 1.00 (0.35)a |
| EDBC | Ap | 7.1 (1.0)a | 9.4 (1.3)a | 0.76 (0.14)a |
| CDBC | Apk | 7.3 (0.2)a | 10.0 (3.0)a | 0.86 (0.11)a |
| | <i>Horizon 2</i> | | | |
| HLG | Aeg | 6.5 (0.2)a | 9.7 (4.0)a | 0.92 (0.30)a |
| EDBC | Ae | 9.8 (0.4)a | 16.7 (5.0)a | 1.03 (0.54)a |
| CDBC | Bmk | 8.2 (0.4)a | 13.2 (4.0)a | 0.70 (0.49)a |
| | <i>Horizon 3</i> | | | |
| HLG | Btg | 11.9 (0.5)a | 20.6 (5.8)a | 1.71 (0.97)a |
| EDBC | Bt | 15.9 (0.2)a | 22.4 (9.5)a | 1.83 (0.43)a |
| CDBC | Cca | 11.3 (0.5)a | 13.4 (5.5)a | 1.28 (0.60)a |

†HLG: Humic Luvic Gleysol; EDBC: Eluviated Dark Brown Chernozem; CDBC: Calcareous Dark Brown Chernozem

‡ ΣC_{\min} : total carbon mineralization; OC: organic carbon

§Columns have mean values for mineralization parameters with standard deviation in parentheses

¶Mean values followed by the same letter within a column for a given horizon are not significantly different according to Tukey's test ($P < 0.05$)

C_o : potential carbon mineralization; k_c : carbon mineralization rate constant; $C_o k_c$: initial potential carbon mineralization rate

Correlations between the C mineralization parameters and soil properties were completed on the data grouped in two different ways. First, correlations were made for each horizon across all three soil classes combined to determine the strength of the non-soil-specific relationships (Table 3.5). Second, correlations were assessed across the three horizons within a given soil class to determine the soil-specific relationships, and then to compare these across the three soil classes (Table 3.6).

Correlations between C mineralization and soil factors for each horizon, across all three soil classes, showed that the sand fraction did not correlate with any of the C mineralization parameters. No significant correlations were found between the clay fraction in horizons 1 and 3, whereas the clay fraction in horizon 2 showed a significant negative correlation ($P < 0.05$, Table 3.5) with most of the mineralization parameters. The silt fraction showed a very significant positive correlation ($P < 0.01$, Table 3.5) with rC_{\min} and a significant positive correlation ($P < 0.05$, Table 3.5) with $C_o k_c$ and rC_{\min} in horizons 2 and 3, respectively.

Table 3.5 Pearson's correlation coefficient between carbon mineralization parameters and soil horizon properties.

| Horizon no.† | Parameter‡ | Sand | Silt | Clay | pH | Organic carbon | Inorganic carbon | Total nitrogen | C:N ratio§ |
|--------------|-------------|--------|---------|---------|---------|----------------|------------------|----------------|------------|
| 1 | rC_{\min} | 0.331 | -0.037 | -0.398 | -0.649* | 0.503 | -0.357 | 0.512 | -0.156 |
| | C_o | 0.155 | -0.328 | 0.102 | -0.175 | 0.319 | -0.061 | 0.246 | 0.085 |
| | k_C | 0.256 | -0.003 | -0.332 | -0.061 | 0.288 | 0.102 | 0.479 | -0.533 |
| | $C_o k_C$ | 0.227 | -0.301 | -0.018 | -0.214 | 0.435 | -0.022 | 0.431 | -0.116 |
| 2 | rC_{\min} | 0.178 | 0.791** | -0.636* | -0.650* | 0.033 | -0.454 | 0.677* | -0.336 |
| | C_o | -0.558 | 0.279 | 0.343 | 0.393 | 0.581* | -0.424 | -0.076 | 0.694* |
| | k_C | 0.391 | 0.414 | -0.604* | -0.572 | -0.043 | -0.106 | 0.726** | -0.441 |
| | $C_o k_C$ | 0.221 | 0.691* | -0.606* | -0.601* | 0.090 | -0.344 | 0.780** | -0.325 |
| 3 | rC_{\min} | 0.030 | 0.645* | -0.311 | -0.571 | 0.288 | -0.653* | -0.468 | 0.065 |
| | C_o | 0.196 | 0.110 | -0.275 | 0.248 | -0.181 | 0.105 | 0.772** | -0.440 |
| | k_C | 0.201 | 0.045 | -0.254 | -0.533 | 0.139 | -0.499 | -0.605* | 0.120 |
| | $C_o k_C$ | 0.274 | 0.284 | -0.441 | -0.611* | 0.183 | -0.645* | -0.532 | 0.034 |

†1, first horizon of each soil; 2, second horizon of each soil; 3, horizon of each soil

rC_{\min} : carbon mineralization rate; C_o : potential carbon mineralization; k_C : carbon mineralization rate constant; $C_o k_C$: initial potential carbon mineralization rate

§C:N ratio, carbon-nitrogen ratio;

* = significant at $P < 0.05$; ** = highly significant at $P < 0.01$

Table 3.6 Pearson's correlation coefficient between carbon mineralization parameters and properties of three wetland soils.

| Soil type† | Parameter‡ | Sand | Silt | Clay | pH | Organic carbon | Inorganic carbon | Total nitrogen | C:N ratio§ |
|------------|-------------|---------|---------|----------|---------|----------------|------------------|----------------|------------|
| HLG | rC_{\min} | 0.803** | -0.179 | -0.680* | 0.181 | 0.898** | 0.73** | 0.911** | 0.542 |
| | C_o | 0.754** | -0.299 | -0.576 | 0.215 | 0.771** | 0.594* | 0.766** | 0.499 |
| | k_C | -0.159 | 0.523 | -0.100 | 0.305 | 0.169 | -0.123 | 0.196 | 0.023 |
| | $C_o k_C$ | 0.741** | -0.199 | -0.611* | 0.262 | 0.823** | 0.596* | 0.823** | 0.514 |
| EDBC | rC_{\min} | 0.562 | 0.566 | -0.726** | -0.107 | 0.952** | 0.076 | 0.954** | 0.744** |
| | C_o | 0.533 | 0.572 | -0.701* | -0.080 | 0.934** | 0.130 | 0.938** | 0.699** |
| | k_C | 0.308 | -0.297 | -0.191 | -0.232 | -0.007 | -0.091 | 0.016 | 0.042 |
| | $C_o k_C$ | 0.599* | 0.512 | -0.743** | -0.176 | 0.913** | 0.093 | 0.933** | 0.696* |
| CDBC | rC_{\min} | 0.713** | 0.655* | -0.828** | -0.591* | 0.585* | -0.656* | -0.102 | -0.046 |
| | C_o | 0.505 | 0.782** | -0.688* | -0.249 | 0.690* | -0.816** | 0.180 | 0.150 |
| | k_C | 0.660* | 0.088 | -0.601* | -0.585* | 0.342 | -0.102 | -0.380 | -0.209 |
| | $C_o k_C$ | 0.757** | 0.591* | -0.846** | -0.552 | 0.660* | -0.613* | -0.116 | -0.060 |

†HLG: Humic Luvic Gleysol; EDBC: Eluviated Dark Brown Chernozem; CDBC: Calcareous Dark Brown Chernozem

‡ rC_{\min} : carbon mineralization rate; C_o : potential carbon mineralization rate; k_C : carbon mineralization rate constant; $C_o k_C$: initial potential carbon mineralization rate

§CN ratio, carbon-nitrogen ratio

* = significant at $P < 0.05$; ** = highly significant at $P < 0.01$

In horizons 1 and 2, pH showed a significant negative correlation with rC_{\min} , and a similar correlation between pH and $C_o k_C$ in horizons 2 and 3. Organic C showed a significant positive correlation ($P < 0.05$, Table 3.5) with C_o in horizon 2, while IC showed a significant negative correlation ($P < 0.05$, Table 3.5) with rC_{\min} and $C_o k_C$ in horizon 3. Nitrogen showed a significant positive correlation with rC_{\min} and a highly significant positive correlation with k_C and $C_o k_C$ in horizon 2, while in horizon 3 it showed a similar correlation with C_o but a significant negative correlation ($P < 0.05$, Table 3.5) with k_C .

When the same correlations were examined for individual soil classes based on their respective horizons, the correlations within the soil classes was very different from what was observed for the individual horizons with all soil classes combined; generally the correlation coefficients typically were higher, and more correlations were significant. Clay was negatively correlated ($P < 0.05$, Table 3.6) to rC_{\min} in all three soil classes. Sand showed a significant ($P < 0.05$, Table 3.6) to highly significant positive correlation ($P < 0.01$, Table 3.6) with most of the mineralization parameters in HLG and CDBC. Silt was significantly ($P < 0.05$, Table 3.6) related to rC_{\min} and $C_o k_C$, and showed a highly significant positive correlation ($P < 0.01$, Table 3.6) with C_o in the CDBC soils but not in the other two classes.

Inorganic C showed a highly significant positive correlation ($P < 0.01$, Table 3.6) with rC_{\min} and a significant positive correlation ($P < 0.05$, Table 3.6) with C_o and $C_o k_C$ in the HLG. In the CDBC, there was a significant negative correlation ($P < 0.05$, Table 3.6) with rC_{\min} and $C_o k_C$, and a highly significant negative correlation ($P < 0.01$, Table 3.6) with C_o . There was no correlation between IC and any of the mineralization parameters in the EDBC.

Organic C and N showed a highly significant positive correlation ($P < 0.01$, Table 3.6) with all the parameters except k_C in both the HLG and EDBC, while OC showed a significant positive correlation ($P < 0.05$, Table 3.6) for the same parameters in the CDBC. The EDBC was the only soil class where C:N ratio showed a significant positive correlation ($P < 0.05$, Table 3.6) with almost all the mineralization parameters.

3.3.3 Nitrogen dynamics

Generally, the surface horizon had the highest NO_3^- -N supply rate, estimated using the PRSTM probes, compared to the second and third horizons of the three soils (Table 3.7). Nitrate-N supply rate in the surface horizons ranged from 20 to 40 $\mu\text{g cm}^{-2} \text{wk}^{-1}$. Nitrate-N supply rate in the surface soils of the HLG was significantly greater than in the CDBC (Table 3.7) and the EDBC soils were not statistically different from either of the other two. There were no significant differences in the NO_3^- -N supply rate of the second and third horizons of the three soils. There were no significant differences in the NH_4^+ -N supply rate in the surface soils of the three soils (Table 3.7). Similarly, there were no significant differences in NH_4^+ -N supply rate in the second and third horizons. The rates varied between < 1 and 2 $\mu\text{g cm}^{-2} \text{wk}^{-1}$. Overall, NH_4^+ -N supply rates were lower than those for NO_3^- -N, suggesting that initial (i.e., pre-incubation) NO_3^- -N levels were presumably relatively high, assuming that NH_4^+ -N was the substrate for nitrification, or that mineralized NH_4^+ -N was nitrified before it diffused to the surface of the cation exchange membrane.

Table 3.7 Nutrient supply rate (NSR) using plant root simulator (PRSTM) probes.

| Soil type† | Horizon | Nitrate-N | Ammonium-N |
|------------------|---------|---|-------------|
| | | <hr/> $\mu\text{g cm}^{-2} \text{ wk}^{-1}$ <hr/> | |
| <i>Horizon 1</i> | | | |
| HLG | Ap | 40.6 (10)a‡ | 1.4 (0.4)a§ |
| EDBC | Ap | 32.9 (11)ab | 2.0 (0.7)a |
| CDBC | Apk | 20.6 (7)b | 1.8 (1.0)a |
| <i>Horizon 2</i> | | | |
| HLG | Aeg | 21.5 (11)a | 1.2 (1.0)a |
| EDBC | Ae | 16.7 (7)a | 1.9 (1.0)a |
| CDBC | Bmk | 15.1 (4)a | 1.3 (0.7)a |
| <i>Horizon 3</i> | | | |
| HLG | Btg | 14.7 (4)a | 0.6 (0.1)a |
| EDBC | Bt | 13.0 (4)a | 2.0 (1.0)a |
| CDBC | Cca | 8.8 (3)a | 1.1 (1.0)a |

†HLG: Humic Luvic Gleysol; EDBC: Eluviated Dark Brown Chernozem; CDBC: Calcareous Dark Brown Chernozem

‡Columns have mean values with standard deviation in parentheses

§Mean values followed by the same letter within a column for a given horizon are not significantly different according to Tukey's test ($P < 0.05$)

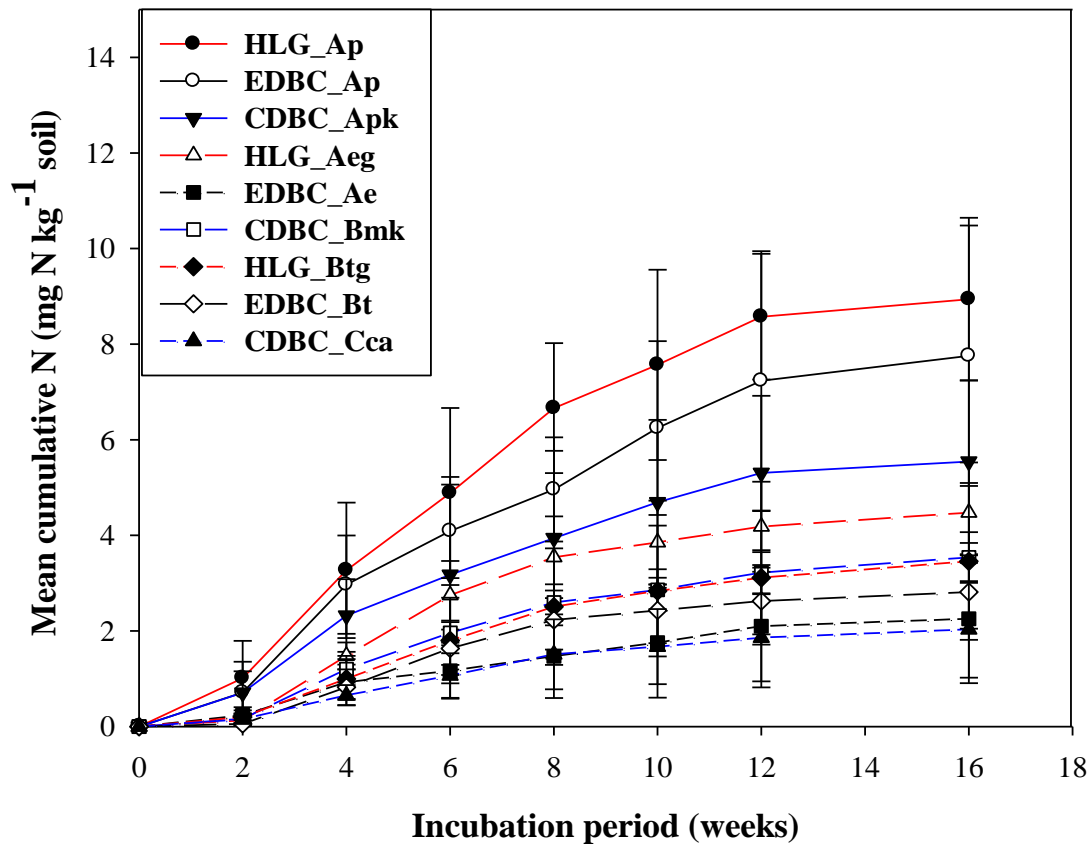


Figure 3.3 Mean cumulative N mineralization in three wetland soils at SDNWA.

HLG, Humic Luvic Gleysol; EDBC, Eluviated Dark Brown Chernozem; CDBC, Calcareous Dark Brown Chernozem; Errors bars are for standard deviation (n=4)

Mean cumulative N mineralization estimated using an incubation-extraction technique was highest in the surface horizons (Figure 3.3) compared to the lower horizons. The surface horizon of the HLG showed the highest mean cumulative N mineralization over the 16 wk incubation period. There was considerable overlap at all times in mean cumulative N mineralization in the second and third horizons of the three soils. However, in all the three soils, there was a lag during the first two weeks of incubation following the initial extraction which presumably removed initial inorganic N from the soil system. Cumulative N mineralization increased after this lag phase and then tapered off from 12 to 16 wk in the first horizons. In the case of the second and third horizons, the cumulative N levels tapered off from the 8 to 16 wk (Figure 3.3).

Table 3.8 Total nitrogen mineralization (ΣN_{\min}), N mineralization rate (rN_{\min}), mean potential N mineralization (N_o), mineralization rate constant (k_N) and initial potential N mineralization rate ($N_o k_N$).

| Soil type† | Horizon | ΣN_{\min} mg N kg ⁻¹ soil | rN_{\min} mg N kg ⁻¹ soil wk ⁻¹ | N_o mg N kg ⁻¹ soil | k_N wk ⁻¹ | $N_o k_N$ mg N kg ⁻¹ soil wk ⁻¹ |
|------------------|---------|---|---|-------------------------------------|---------------------------|---|
| <i>Horizon 1</i> | | | | | | |
| HLG | Ap | 10.01 (5.2)a‡ | 0.625 (0.32)a§ | 9.77 (5.9)b | 0.095 (0.057)a | 1.29 (1.08)a |
| EDBC | Ap | 7.94 (2.7)a | 0.496 (0.17)a | 8.09 (2.9)b | 0.078 (0.059)a | 0.57 (0.40)a |
| CDBC | Apk | 5.54 (1.7)a | 0.346 (0.11)a | 28.0 (19.0)a | 0.018 (0.008)a | 0.91 (0.23)a |
| <i>Horizon 2</i> | | | | | | |
| HLG | Aeg | 4.47 (1.1)a | 0.280 (0.07)a | 6.77 (2.6)a | 0.061 (0.012)a | 0.42 (0.16)a |
| EDBC | Ae | 4.06 (1.3)a | 0.253 (0.08)a | 5.94 (1.9)a | 0.099 (0.026)a | 0.57 (0.17)a |
| CDBC | Bmk | 3.54 (0.5)a | 0.221 (0.03)a | 5.69 (2.9)a | 0.080 (0.036)a | 0.38 (0.07)a |
| <i>Horizon 3</i> | | | | | | |
| HLG | Btg | 3.46 (1.6)a | 0.216 (0.10)a | 6.30 (3.2)a | 0.056 (0.017)a | 0.32 (0.14)a |
| EDBC | Bt | 2.81 (0.8)a | 0.176 (0.05)a | 4.04 (1.3)a | 0.089 (0.034)a | 0.35 (0.13)a |
| CDBC | Cca | 2.03 (1.0)a | 0.127 (0.06)a | 4.75 (2.4)a | 0.051 (0.036)a | 0.19 (0.11)a |

†HLG: Humic Luvic Gleysol; EDBC: Eluviated Dark Brown Chernozem; CDBC: Calcareous Dark Brown Chernozem

‡Columns have mean values for mineralization parameters with standard deviation in parentheses

§Mean values followed by the same letter within a column for a given horizon are not significantly different according to Tukey's test ($P < 0.05$)

Within horizons, there were no significant differences in the amount of N mineralized during the 16 wk of aerobic incubation (Table 3.8). There were no significant differences ($P < 0.05$) in ΣN_{\min} , rN_{\min} , k_N or $N_o k_N$ across the three horizons of the three soils. The mean N_o value for horizon 1 of CDBC was significantly greater than for HLG and EDBC (Table 3.8). Calculated N_o values for all replicates of horizon 1 of CDBC except one were higher than values for horizon 1 of HLG and EDBC. The high values could be due to the inverse relationship between N_o and k_N which is intrinsic in the first order model. This probably introduced artifacts in the experimental data of horizon 1 of CDBC which possibly influenced the estimation of the N_o values for this horizon.

As in the case of C mineralization, N mineralization parameters were normalized against the total N present in the soil (Table 3.9). The values for ΣN_{\min} :soil N ratio for the three horizons were not significantly different. The values ranged from 2 to 4 mg of potentially mineralizable N g⁻¹ total N, representing 0.2 to 0.4% of total N mineralized. In the case of N_o :N, the ratio for

Table 3.9 Normalized nitrogen mineralization parameters with soil nitrogen.

| Soil type† | Horizon | $\Sigma N_{\min}:N‡$ | $N_o:N$ | $N_o k_N:N\#$ |
|------------|------------------|------------------------|---------------|---------------------------------------|
| | | mg N g ⁻¹ N | | mg N g ⁻¹ wk ⁻¹ |
| | <i>Horizon 1</i> | | | |
| HLG | Ap | 2.78 (2.0)a§ | 2.96 (1.2)b¶ | 0.337 (0.450)a |
| EDBC | Ap | 2.59 (0.7)a | 5.72 (2.7)b | 0.206 (0.170)a |
| CDBC | Apk | 2.27 (1.4)a | 13.00 (10.8)a | 1.286 (0.870)a |
| | <i>Horizon 2</i> | | | |
| HLG | Aeg | 2.83 (0.8)a | 4.68 (2.3)a | 0.294 (0.150)a |
| EDBC | Ae | 3.63 (1.4)a | 5.07 (1.1)a | 0.505 (0.190)a |
| CDBC | Bmk | 3.49 (0.9)a | 5.84 (3.9)a | 0.369 (0.040)a |
| | <i>Horizon 3</i> | | | |
| HLG | Btg | 3.12 (1.4)a | 5.60 (2.5)a | 0.291 (0.110)a |
| EDBC | Bt | 3.37 (0.9)a | 4.84 (1.5)a | 0.415 (0.170)a |
| CDBC | Cca | 3.22 (1.4)a | 8.50 (4.6)a | 0.251 (0.180)a |

†HLG: Humic Luvic Gleysol; EDBC: Eluviated Dark Brown Chernozem; CDBC: Calcareous Dark Brown Chernozem

‡ ΣN_{\min} : total nitrogen mineralization; N: total nitrogen

§Columns have mean values for mineralization parameters with standard deviation in parentheses

¶Mean values followed by the same letter within a column are not significantly different according to Tukey's test ($P < 0.05$)

$N_o k_N:N$: N_o : potential nitrogen mineralization; k_N : N mineralization rate constant; $N_o k_N$: initial potential N mineralization rate

horizon 1 of CDBC was significantly greater than in HLG and CDBC (Table 3.9) with N_o ranging from 0.03 to 1.30% of the total N that could be potentially mineralized in the surface soils. Horizons 2 and 3 had ranges from 0.05 to 0.09% of total N. Hence on the basis of this, the potential value of N_o could be about twice that of ΣN_{\min} . Unlike $N_o:N$, which showed differences among the surface horizons, no significant differences were observed across all three horizons when $N_o k_N:N$ was used (Table 3.9).

Correlations for each horizon across all three soil classes showed that in horizons 1 and 2 of the three soils, there were no significant correlations of the N mineralization parameters with any of the measured soil properties (Table 3.10). In horizon 3, however, pH showed a significant negative correlation with rN_{\min} and $N_o k_N$ ($P < 0.05$). Organic C had a significant positive correlation ($P < 0.05$) with rN_{\min} . As with C mineralization, the correlations across the three horizons for each soil class showed more distinct correlations between soil properties and N mineralization. The clay fraction of HLG soils showed a significant negative correlation ($P < 0.05$, Table 3.11) with rN_{\min} , while in the EDBC soils the correlation was highly significantly

Table 3.10 Pearson's correlation coefficient between nitrogen mineralization parameters and soil horizon properties.

| Horizon no.† | Parameter‡ | Sand | Silt | Clay | pH | Organic carbon | Inorganic carbon | Total nitrogen | C:N ratio§ |
|--------------|-------------------------------|--------|--------|--------|---------|----------------|------------------|----------------|------------|
| 1 | rN _{min} | 0.389 | -0.364 | -0.162 | -0.342 | -0.245 | 0.061 | -0.034 | -0.576 |
| | N _o | 0.100 | -0.423 | 0.246 | 0.483 | -0.298 | 0.188 | -0.170 | -0.186 |
| | k _N | 0.185 | -0.281 | 0.017 | 0.124 | -0.274 | -0.045 | -0.266 | 0.103 |
| | N _o k _N | 0.168 | -0.533 | 0.258 | 0.480 | -0.404 | 0.152 | -0.261 | -0.191 |
| 2 | rN _{min} | 0.287 | 0.331 | -0.459 | -0.228 | 0.234 | -0.389 | 0.495 | -0.036 |
| | N _o | -0.064 | 0.381 | -0.169 | -0.317 | -0.274 | -0.250 | -0.146 | -0.236 |
| | k _N | -0.124 | -0.415 | 0.361 | 0.079 | -0.022 | 0.108 | -0.311 | 0.156 |
| | N _o k _N | -0.106 | 0.070 | 0.055 | -0.314 | -0.217 | -0.285 | -0.325 | -0.057 |
| 3 | rN _{min} | 0.423 | 0.064 | -0.520 | -0.609* | 0.659* | -0.403 | -0.422 | 0.341 |
| | N _o | 0.324 | 0.038 | -0.394 | -0.224 | 0.399 | -0.100 | 0.294 | -0.070 |
| | k _N | -0.073 | -0.063 | 0.112 | -0.287 | -0.008 | -0.222 | -0.558 | 0.125 |
| | N _o k _N | 0.367 | -0.073 | -0.396 | -0.648* | 0.480 | -0.436 | -0.510 | 0.231 |

†1: first horizon of each soil; 2: second horizon of each soil; 3: third horizon of each soil

‡rN_{min}: nitrogen mineralization rate; N_o:potential nitrogen mineralization; k_N: nitrogen mineralization rate constant; N_ok_N: initial potential nitrogen mineralization rate

§C:N carbon nitrogen ratio

*= significant at P < 0.05; **= highly significant at P < 0.01

Table 3.11 Pearson's correlation coefficient between nitrogen mineralization parameters and properties of three wetland soils.

| Soil type† | Parameter‡ | Sand | Silt | Clay | pH | Organic carbon | Inorganic carbon | Total nitrogen | C:N ratio§ |
|------------|-------------------------------|---------|--------|----------|--------|----------------|------------------|----------------|------------|
| HLG | rN _{min} | 0.836** | -0.432 | -0.589* | 0.260 | 0.556 | 0.621* | 0.577* | 0.480 |
| | N _o | 0.585* | -0.485 | -0.325 | 0.138 | 0.158 | 0.370 | 0.163 | 0.320 |
| | k _N | 0.486 | -0.135 | -0.399 | 0.169 | 0.272 | 0.592* | 0.336 | 0.075 |
| | N _o k _N | 0.592* | -0.405 | -0.370 | 0.193 | 0.204 | 0.533 | 0.252 | 0.168 |
| EDBC | rN _{min} | 0.639* | 0.455 | -0.762** | -0.283 | 0.819** | 0.440 | 0.871** | 0.586* |
| | N _o | 0.481 | 0.507 | -0.629* | -0.485 | 0.617* | 0.304 | 0.646* | 0.595* |
| | k _N | -0.180 | -0.159 | 0.225 | 0.276 | -0.277 | -0.242 | -0.344 | -0.179 |
| | N _o k _N | 0.209 | 0.133 | -0.243 | -0.009 | 0.205 | -0.227 | 0.117 | 0.360 |
| CDBC | rN _{min} | 0.452 | 0.654* | -0.592 | -0.548 | 0.485 | -0.653* | -0.371 | 0.173 |
| | N _o | 0.745** | -0.507 | -0.819** | -0.529 | 0.613* | -0.635* | 0.008 | -0.061 |
| | k _N | -0.062 | -0.118 | 0.089 | -0.231 | 0.561 | -0.071 | -0.599 | 0.536 |
| | N _o k _N | 0.723* | 0.485 | -0.793** | -0.534 | 0.643* | -0.642* | -0.062 | 0.004 |

†HLG, Humic Luvic Gleysol; EDBC, Eluviated Dark Brown Chernozem; CDBC, Calcareous Dark Brown Chernozem

‡rN_{min}: nitrogen mineralization rate; N_o:potential nitrogen mineralization; k_N: nitrogen mineralization rate constant; N_ok_N: initial potential nitrogen mineralization rate

§C:N carbon nitrogen ratio

*: significant at P < 0.05; **: highly significant at P < 0.01

negative with rN_{\min} and significantly negative with N_o . With the CDBC soils, the clay fraction showed a very significant negative correlation ($P < 0.01$, Table 3.11) with N_o and $N_o k_N$.

The sand fraction of the HLG showed a highly significant positive correlation (Table 3.11) with rN_{\min} , while the correlation with N_o and $N_o k_N$ was significantly positive. The sand fraction of the EDBC showed a significant positive correlation (Table 3.11) with rN_{\min} , while that of the CDBC showed a highly significant positive correlation (Table 3.11) with N_o and a significant positive correlation with $N_o k_N$.

Organic C levels of the HLG were not correlated with any N mineralization parameter (Table 3.11). For the EDBC soils, OC showed a highly significant positive correlation with rN_{\min} and a significant positive correlation with N_o , while a significant positive correlation was shown with N_o and $N_o k_N$ in CDBC. There was a positive correlation between N and rN_{\min} in HLG and EDBC soils in addition to significant positive correlation between N and N_o in the latter class. In the case of CDBC, there was no correlation between N and any mineralization parameter. It was only in the EDBC soil class that C:N ratio showed a significant positive correlation with two mineralization parameters (rN_{\min} and N_o). No correlation was observed with the other two soils. Inorganic C had a significant positive correlation (Table 3.11) with rN_{\min} and k_N in HLG but a significant negative correlation was shown with rN_{\min} , N_o and $N_o k_N$ for the CDBC soils. There was no significant correlation between pH of the three soils with any N mineralization parameter.

Ammonium–N levels were below detection limits after the second week of aerobic incubation. As a result, data obtained for N mineralization in the 16 wk study were based entirely on NO_3^- -N.

3.4 Discussion

The research design used in this study allows comparisons of C and N attributes at different depths in the soil profile and among the three soil classes. Generally the differences with depth within each soil class were more striking (but also better known from previous studies) than those associated with the main factor examined i.e. soil class. Although the three classes of soils are known to have different genetic pathways, most of the C and N mineralization assays used in this study showed few significant differences among the three soil groups, when mineralization parameters were normalized against organic C and N levels.

This study showed that there are clear changes in C and N mineralization assays with depth with most activity concentrated in the topsoil (horizon 1). Higher total C mineralization in the surface than lower horizons have been reported by others (Persson et al., 2000; Kruse et al., 2004). In the present study, the higher levels of OC in the surface horizons might not be the only cause of the high C mineralization. Differences in the quality of the SOM may also have influenced mineralization. For example, there could be more labile C in the surface horizons, especially in the HLG, compared to the other soils. Most of the easily decomposed SOM, or the light fraction, is usually incorporated in the topsoil where the turnover rate is very high. On the other hand, the lower soil layers usually have the heavy fraction which decomposes slowly and hence a lower turnover rate (Alvarez and Alvarez, 2000; Yun-Feng and Zu-Cong, 2006). Janzen et al. (1992) and Rey et al. (2005) attributed the faster mineralization of light fraction compared to the heavy fraction to the former's labile nature and lack of stabilization by clay minerals. This, they concluded, exposes the light fraction to microbial decomposition without difficulty. However, in this study differences in C and N mineralization parameters typically disappeared when data were normalized against organic C and total N respectively. This suggests that quantity rather than quality of organic materials largely controlled the mineralization parameters.

Nitrogen mineralization also decreased with depth in all the soils (as with cumulative C mineralization), with the HLG soils consistently showing the highest values and CDBC soils the lowest. All the other N mineralization parameters (rN_{\min} , k_N and N_0k_N) except N_o , showed a similar pattern. Cumulative N mineralization increased in all the soils after an initial lag phase

(Figure 3.3). Lags have been observed in the initial phase of N mineralization by many researchers (Stanford and Smith, 1972; Ellert and Bettany, 1988). The observed lag phase could be attributed to the relatively low N contents of the soils and the resultant N immobilization by microbial biomass (Nosshi et al., 2007). Similar observations were made by Heumann et al (2002) in their study on net N mineralization at a temperature of 35 °C. However, in other studies N mineralization was very rapid in the first two weeks (Haney et al., 2004; Sharifi et al., 2007) indicating the presence of more organic N in the labile fraction of SOM for microbial use (Jalil et al., 1996; Curtin and Wen, 1999).

Comparisons between different incubation studies can be confounded by the effects of the duration of the incubation. Short duration incubation can result in higher mineralization rates than long duration incubation. The mineralization rates in this study for the topsoils ranged from 8.7 to 13.4 mg CO₂-C kg⁻¹ d⁻¹ during a 16 d incubation. Ahn et al. (2009) studied C mineralization in topsoils of comparable soils under various land uses and found that the mineralization rates ranged from 6.7 to 8.3 mg CO₂-C kg⁻¹ d⁻¹ in an 87 d incubation. In fact, Ahn et al. (2009) observed a high rC_{min} in the early days of incubation and the rate became more stable over time as the mineralization progressed. This suggests a change from a labile to more slowly decomposing fraction (Paul et al., 2001) which presumably was not reached in this study. Goebel et al. (2009) reported two stages of C loss as incubation progresses. Like others (Rey et al., 2005; Zhao et al., 2008) they also observed an initial flush in mineralization which tapered off and stabilized with time. The observed variations in C mineralization during incubation while implying the presence of different C pools also shows that these pools differ in C bioavailability in the soils during incubation (Zhang et al., 2007).

As with C mineralization, a short term incubation study for N mineralization using PRSTM probes showed higher NSR, in terms of NO₃⁻-N, for horizon 1 than for horizons 2 and 3 of the three soils (Table 3.7). This could be attributed to higher OC, and thus SOM content of the surface horizons. This could also account for the high NSR as a result of more NO₃⁻ ion accumulation on the PRSTM probes in horizon 1 of HLG compared to the EDBC and CDBC. Levels of N in horizons 2 and 3 of the three soils were low because of the low levels of OC in these horizons. The differences observed in the NSR between HLG and the other two soils,

particularly CDBC could also be attributed to higher OC and N in the former soils compared with the latter (Qian and Schoenau, 1995). The NSR, in terms of $\text{NH}_4^+\text{-N}$, was low and could be the result of a faster conversion to $\text{NO}_3^-\text{-N}$ in the presence of adequate aeration in the incubating Mason jars. This presumes that nitrification occurred at microsites before $\text{NH}_4^+\text{-N}$ diffused to the cation exchange membrane and that the PRS^{TM} probes thereby underestimated $\text{NH}_4^+\text{-N}$ mineralization rates. Total NSR was, however, obtained from the addition of the two mineralized forms of N, as suggested by some researchers (Maynard et al., 1985) and thus any underestimation of the $\text{NH}_4^+\text{-N}$ mineralization rates would be accounted for by the enhanced $\text{NO}_3^-\text{-N}$ mineralization. Total NSR also serves as an index of N mineralization (Qian and Schoenau, 1995).

The C:N ratios of the three soils were narrow, with all values < 10 (Table 3.2). The C:N ratio of SOM is a widely used index for predicting mineralization of any organic material. Typically, C:N ratios of organic material beyond 20:1 and 30:1 are known to encourage immobilization rather than mineralization while ratios lower than these ranges are associated with enhanced mineralization (Stevenson and Cole, 1999b). Similar ranges of values to the current study were found by Anderson (1972) when he examined organic matter properties of some soils including those of the grasslands of Saskatchewan. One reason Anderson (1972) gave for the low C:N ratios was that N contributed from ammonium (NH_4^+) was fixed by the clay. The fixation of NH_4^+ by clay minerals occurs more in the subsoil or lower horizons than in the surface or topsoil because of the high clay levels in the subsoil. Usually, soils with 2:1 clay minerals account for 20 to 40% of N in the subsoil and only 5 to 10% N in the topsoil (Brady and Weil, 2008). These could be responsible for NH_4^+ fixation in the soils leading to the low C:N ratios. The low C:N ratios could also be explained by the likelihood of having microbial-rich material in addition to accumulated labile pool of organic compounds high in N, such as amino acids, and other non-labile organic N compounds at depth where there is little or no decomposition pressure from microorganisms (D.W. Anderson, pers. comm.).

Given the observed narrow C:N ratios in this study, it would have been expected that C mineralization in all the horizons should be high. This was not the case, however, and one reason for the low mineralization is the low OC and N contents of the soils, especially in the lower horizons (Table 3.3) and another reason possibly could be due to lack of indigenous microbes at depth in these horizons. The low levels of OC and N were likely a result of continuous cultivation leading to decreased SOM in the soils. Studies in the agricultural fields of the SDWNA have shown that cultivation results in a significant reduction of C stocks in all landscape elements including the cultivated wetlands (Pennock, 2003; Bedard-Haughn et al., 2006). Some studies have also shown that C:N ratio decreases with decreasing particle size, hence the association of well decomposed SOM with fine size fractions of the soil (Anderson, 1972; Zhang et al., 1988; Christensen, 1992). Differences in the quality of the organic C and N at depth may also contribute to reduced mineralization. Typically, organic materials at depth are more humified (i.e., heavy fraction) and associated with clays and thus may represent more recalcitrant organic materials (Anderson, 1972).

Normalization of C mineralization helps in assessing C_o in relation to amount OC present in the soil (Riffaldi et al., 1996; Raiesi, 2006). Though no significant differences were found in C_o :OC ratios across all three horizons of the three soils there was a general increase with depth from horizon 1 to horizon 3. Several studies have found different C_o :OC ratios depending on soil type and OC content. Riffaldi et al (1996) found that the soils they examined had variable C_o :OC ratios ranging from 0.2 to 2% of the soil OC. Others such as Kruse et al. (2004) and Ahn et al. (2009) have observed values ranging from 0.1 to 1% and 1.1 to 9.6% of OC respectively. The C_o :OC ratios obtained in the current study were within the ranges of 0.94 to 2.24%. The lower C_o :OC ratios in the surface horizons (horizon 1) could be attributed to the presence of more and easily mineralizable C than horizon 3 which had comparatively higher ratios (especially in the HLG and EDBC) indicating the presence of organic material of low mineralizability and/or more protected OC, and hence more C storage (Raiesi, 2006). The pattern was less clear with N_o :N values and there were no significant differences across horizons overall.

The mineralization constants, k_C and k_N , were the least variable of the C and N mineralization parameters since they did not show any significant differences across horizons of all the soils (Table 3.3 and 3.8). The absence of variability in the rate constants observed in this study is in agreement with other researchers (Simard and N'Dayegamiye, 1993; Riffaldi et al., 1996; Sbih et al., 2003). For example, Riffaldi et al. (1996) found k_c values ranging from 0.050 to 0.104 per d while investigating C mineralization in different agricultural soils in a 21 d incubation study. Kaboneka et al. (1997) found that k_C ranged from 0.039 to 0.115 per d in their study while Sbih et al. (2003) found values that ranged from 0.050 to 0.123 per wk. They attributed these narrow ranges in k_C values to mineralization from SOM fraction that had a quick turnover with a first order rate constant. This suggests that C in the soils came from similar compounds in the organic matter (Sbih et al., 2003) which in this case could be low molecular weight organic compounds or that the organic compounds mineralized in the soils were bioavailable to the same degree for microbial decomposition (Riffaldi et al., 1996). The three wetland soils used in this study were all usually put under wheat production and hence subject to similar land use and management. Even though OC contents were different in the three soils, similar organic materials would be generated from the fields and left for decomposition thereby accounting for the non significance in the differences between k_C values across all the horizons. The pattern was the same for similar N mineralization parameters for all three soils.

Given their different genetic pathways it was surprising that SOC levels were not significantly different among the three soil classes (Table 3.2). Studies on native landscapes (Pennock 2003; Landi et al. 2004) and cultivated sites (Pennock and Corre, (2001) have reported higher OC levels in HLG soils compared to other depressional wetland soils. This was attributed to higher moisture conditions in lower slopes and depressions, and consequently more SOM build up in these positions due to suppressed microbial decomposition. The lack of significant differences in the current study may indicate that significant losses of OC have occurred due to cultivation resulting in a homogenization of OC contents across the three soils. Analysis of land use history of SDNWA showed that about 40% of the area, including the study site, has been in cultivation for more than four decades (Van den Bos, 2005).

Differences in genetic class were expressed in the differences in correlations between C and N mineralization parameters (Tables 3.6 and 3.11). There were few significant correlations across all three soil classes but many significant relationships within classes.

Almost all C mineralization parameters showed highly significant positive correlation ($P < 0.01$, Table 3.6) with OC content in the HLG and EDBC soils. The HLG and EDBC soils have relatively higher levels of OC when compared with the CDBC soils. Similar relationships were observed between N in the HLG and EDBC soils and the mineralization parameters. However, fewer N mineralization parameters correlated with OC and N levels of the soils (Table 3.11). This could be due to the low N levels in SOM. Other researchers (Zak et al., 1993; Riffaldi et al., 1996) also found that C mineralization correlated positively with C and N levels in the soil. This shows that SOM is a strong controlling factor on mineralization, since it is the primary reservoir of OC and N in soils.

Particle size, especially sand and clay fractions, was significantly correlated to most mineralization parameters in the HLG and CDBC soils and to a limited extent in EDBC. The sand fraction showed highly significant positive correlations ($P < 0.01$, Tables 3.6) with most of the C mineralization parameters. Sand does not protect SOM from microbial decomposition. In this study, the surface horizons (mainly sandy loams) with over 50% sand content, showed the highest C mineralization. Feller and Beare (1997) reported higher C mineralization in coarse as compared to fine-textured soils. The role played by each particle size fraction in C mineralization largely depends on its mineralization potential, organic C content and actual soil texture (Feller and Beare, 1997). Carbon mineralization potential was significantly higher in horizon 1 of the HLG than in horizon 1 of CDBC but comparable to horizon 1 of EDBC soils though the topsoil textures were all sandy loams. The difference could be attributed to the comparatively higher OC content in horizon 1 of the HLG.

In the case of N mineralization, sand fraction had a highly significant positive correlation ($P < 0.01$, Table 3.11) with few N mineralization parameters in HLG and CDBC. The significant correlation suggests that aeration, associated with higher sand content, may have enhanced N mineralization. Furthermore, sand offers little to no protection against microbial decomposition

of organic materials and thus would be expected to enhance N mineralization. Relatively low levels of N mineralization overall could be attributed to not only low N content but also low mineralizable N levels (Robinson, 1967) in the soils which resulted in microbial immobilization of N in the early stages of decomposition, thus lowering overall N mineralization. The low N mineralization could also be attributed to depletion of labile OC pool in the soil as mineralization progressed (Monreal et al., 1981; Gonzalez-Prieto et al., 1995).

Majority of the C mineralization parameters showed significant ($P < 0.05$, Table 3.6, in the HLG) to highly significant negative correlations ($P < 0.01$, in the EDBC and CDBC soils) with the clay fraction. This suggests that the clay fraction is associated with low C mineralization since clay stabilizes organic C against microbial degradation (Stewart et al., 2008) in proportion to not only the clay content but also silt content of the soil (Hassink, 1997; Puget et al., 1999). Silt and clay content of soils are known to offer physical protection to SOC as the latter forms strong organo–mineral complexes with these particle size fractions (Feller and Beare, 1997; Hassink, 1997; Baldock and Skjemstad, 2000; Six et al., 2002). This occurs through adsorption of positively charged organic molecules onto negatively charged sites of clay and existing organic materials on clay and silt by cation exchange and hydrophobic bonding mechanisms (Zech et al., 1997). Studies have shown that fine to very fine silt fractions are the main components of silt content in soils that stabilize and protect SOM from microbial decomposition (Anderson and Paul, 1984; Christensen and Sorensen, 1985; Gonzalez-Prieto et al., 1996). In contrast, in this study most of the C mineralization parameters in CDBC soils showed a significant ($P < 0.05$, Table 3.6) to highly significant positive correlation ($P < 0.01$, Table 3.6) with the silt fraction. With N mineralization, the correlation was positively significant with rN_{\min} in CDBC. Particle size analysis showed that the silt content of the CDBC soils was dominated by coarse to very coarse silt fractions. These fractions could possibly offer less protection and stabilization of SOM from microbial decomposition and hence the observed positive effect on both C and N mineralization. Similar significant positive correlations between silt fraction and C and N mineralization were also observed by other researchers (Robinson, 1967; Gregorich et al., 1989; Bonde et al., 1992). This suggests that the silt fraction could also be an active centre for C and N mineralization (Robinson, 1967) in soils.

Generally, soil texture determines the aggregation of pores and soil particles. This, in turn, has a significant effect on soil aeration and water availability within the soil. The processes of decomposition and mineralization take place within the pore spaces of the soil where SOM is trapped (Baldock and Skjemstad, 2000). This implies that the size of pores, their distribution and the amount of soil volume they occupy will determine how stable or protected organic matter will be in these pores. According to Franzluebbers (1999) increase in pore size makes the soil more porous hence well aerated and consequently increased mineralization. These changes can be observed as pore size changes from the clay to sand sizes or from fine textures to coarse textures. In this study, the highest C mineralization occurred in horizon 1 of the three soils, which were all sandy loams and the lowest mineralization occurred in horizon 3 of the soils, which were clay loams. This possibly may explain the significant positive correlation of sand with the mineralization parameters and significant negative correlation of clay fraction with the mineralization parameters. Studies by Hassink (1995) and Parfitt and Salt (2001) on size and density fractions of SOM and C and N mineralization in particle size fractions, respectively, also found a high rate of SOM decomposition in coarse-textured soils.

Other factors that could contribute to the observed differences in the C and N mineralization of the soils are their IC, presence of polyvalent cations and pH levels. Inorganic C is associated with CaCO_3 in these soils. Inorganic C in CDBC was negatively correlated with almost all the C and N mineralization parameters while in HLG the correlation was positive (Tables 3.6 and 3.11). There is probably a threshold value of IC below which mineralization can be enhanced and above which mineralization can be suppressed. As a result, the low levels of IC in both HLG and EDBC probably do not offer significant protection against microbial decomposition, but rather enhanced mineralization as evidenced by its significant positive correlation with almost all the mineralization parameters in the case of HLG. Designation of the third horizon of the CDBC as Cca shows that its carbonate content is pedogenic in origin. Numerous studies in the Prairies have shown that the pedogenic carbonate in the soils is dominated by clay-sized calcite (Fuller et al., 1999; Wang and Anderson, 2000). This implies that the IC in CDBC will behave like clay and hence protect and stabilize OC against microbial attack; therefore, increases in IC will be associated with more protection of OC and reduced mineralization. Another factor that could contribute to the low mineralization in the CDBC is

the presence of free Ca^{2+} . As a flocculant, Ca^{2+} has the ability to form complexes with SOM thus protecting it from microbial decomposition. Studies have shown that Ca^{2+} forms organo–Ca complexes with SOM through its flocculating ability, thus stabilizing and protecting it from decomposition (Baldock and Skjemstad, 2000; Six et al., 2002). The high IC levels in CDBC were reflected in its pH, which was also significantly negatively correlated with mineralization in this soil thus implying low mineralization. This observation showed that probably the alkaline conditions in the CDBC soils were not favourable for microbial decomposition of SOM or that the CaCO_3 or free Ca^{2+} in the CDBC was protecting the SOM from decomposition, as stated above. Generally, mineralization is at its optimum at near–neutral pH values (Brady and Weil, 2008a). Regardless of native soil characteristics, soil pH governs SOM decomposition to the extent that the diversity of microbial population involved with the decomposition processes increases from acid to near–neutral or even slightly alkaline conditions (Riffaldi et al., 1996; Brady and Weil, 2008a).

A final point related to the genetic pathways of these soils relate to the poorly understood Btg horizon in the Humic Luvic Gleysols. In the HLG, horizon 3 (Btg) is a layer of uncertain origin and its black appearance gives the impression that it would be rich in OC. However, no differences were observed in OC or any C mineralization parameters for the Aeg and Btg horizons compared to the equivalent horizons in the other two soil classes. The visual lightening of the colour that occurs upon drying of the Btg suggests that the colour difference is not due to differences in OC content, and that field observation is supported by the results of this study.

3.5 Conclusions and Recommendations

Generally, there are differences in genetic properties and in the correlations between soil properties and C and N mineralization among the three soil classes; however, the amount of OC and total N present in the soils and the C and N mineralization parameters were similar, particularly when values were normalized to organic C and N levels. The similarity in the biochemical attributes suggests that whatever differences existed among these soils in their native state (as shown in other studies cited above) either do not translate to differences in mineralization, or these inherent differences have been obliterated by the long cultivation history

of the soils. It is possible that cultivation has caused an overall decrease of OC and total N and has led to a homogenization of values across the three soils. The mineralization assays measured the most labile part of the SOM pool, which reflected in large measure the most recent crop residues inputs. Hence, the cultivation history and cropping practices might have homogenized the C and N attributes of the three soils.

The results of this study would suggest that different approaches to soil management (including stratified sampling of the three soil types for soil test recommendations) are not required, since differences in C and N mineralization were not large. Hence although the genetic differences among these soils are substantial, the effects of these differences on management are probably not agronomically significant.

4.0 REFERENCES

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5.0 APPENDICES

Appendix 5.1 Protocol development

C mineralization

In order to select an incubation period that would give optimum C mineralization, Ap and Btg horizons of soils were incubated at different times – 1 d, 2 d and 3 d – in mason jars. Carbon dioxide gas in the headspace was sampled according to the period of incubation.

For both horizons, cumulative C mineralized (as CO₂ evolved) was highest when the soils were incubated and the gas sampled every 2 d while mineralization was least when the soils were incubated and sampled every 3 d (Figures A5.1a and b). Hence the 2 d period was chosen for the main experiments.

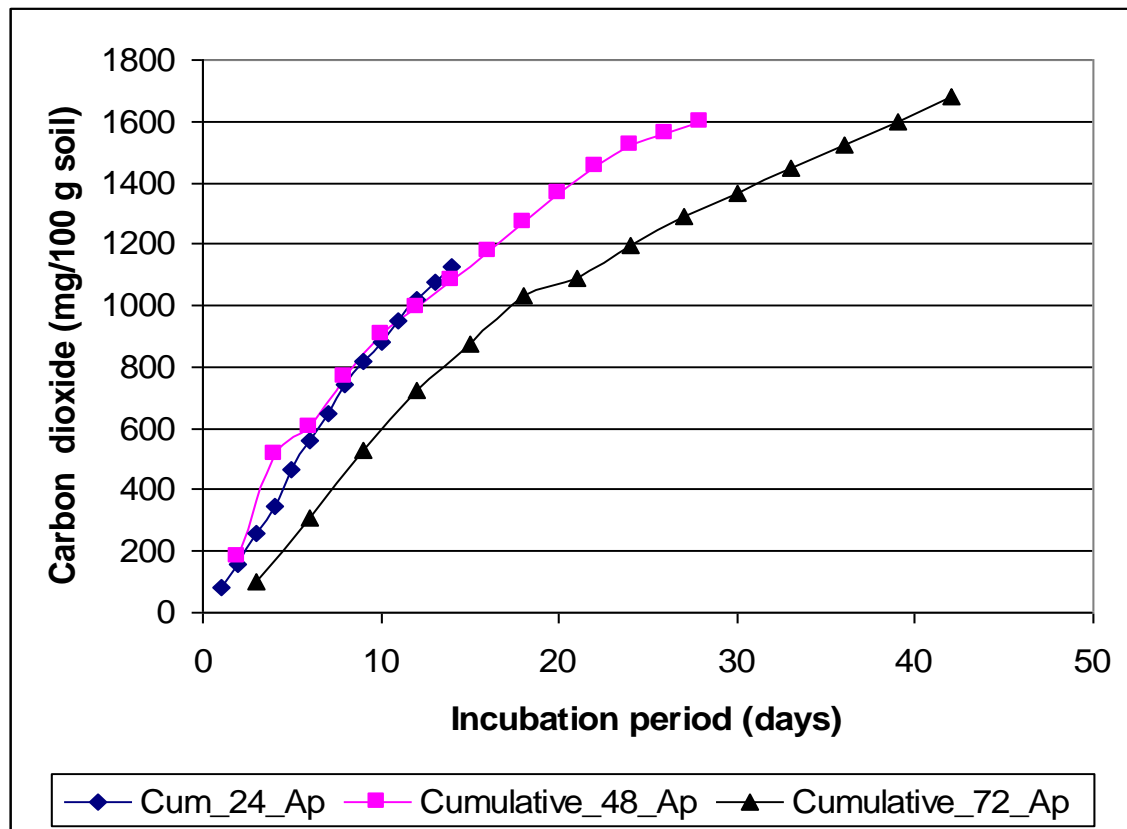


Figure A5.1a Cumulative CO₂ production in Ap horizon at different periods

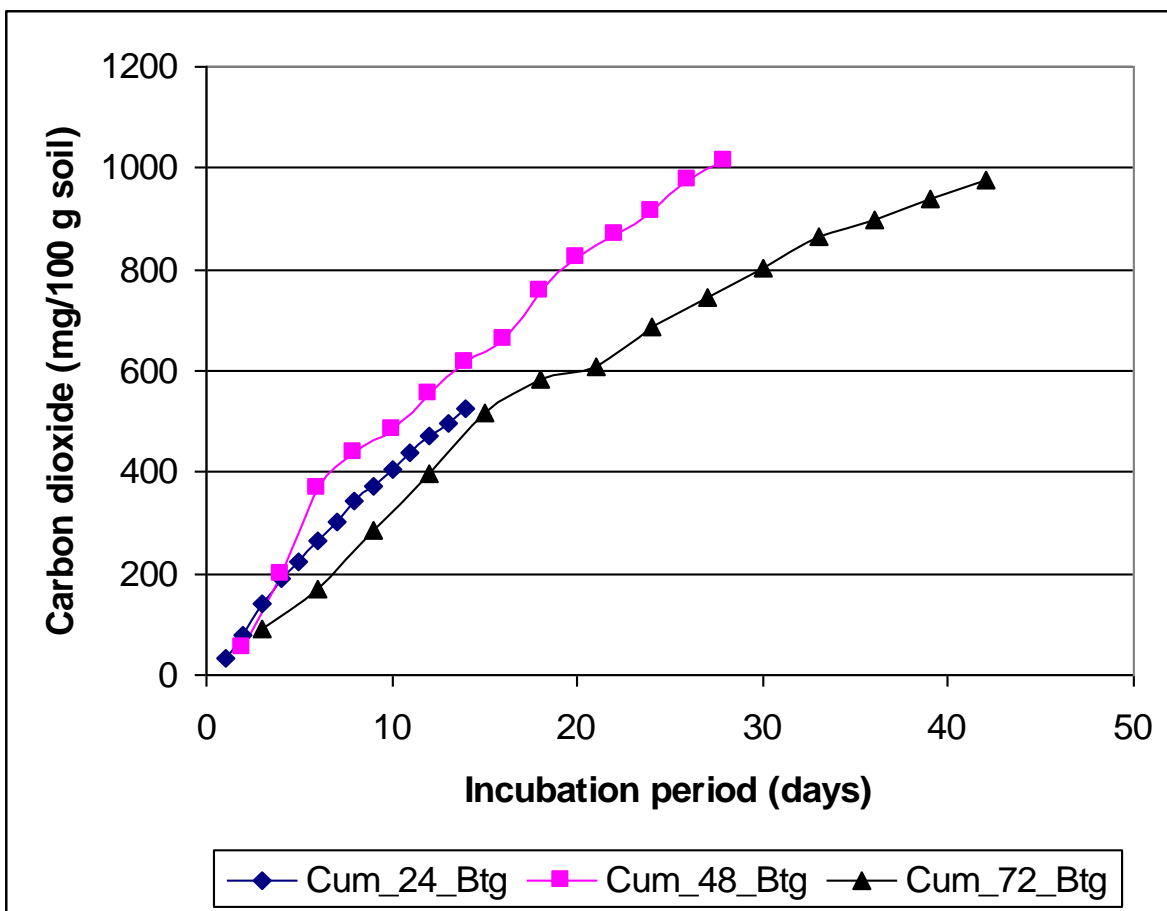


Figure A5.1b Cumulative CO₂ production in Btg horizon at different periods

N mineralization

To determine the N supply rate, plant root simulator (PRSTM) probes were used. The probes were inserted into the soils which were then incubated for 1-d, 4-d, 7-d and 14-d. The 14-d period of incubation resulted in the highest N release in both the Ap and Btg horizons (Figure A5.1c).

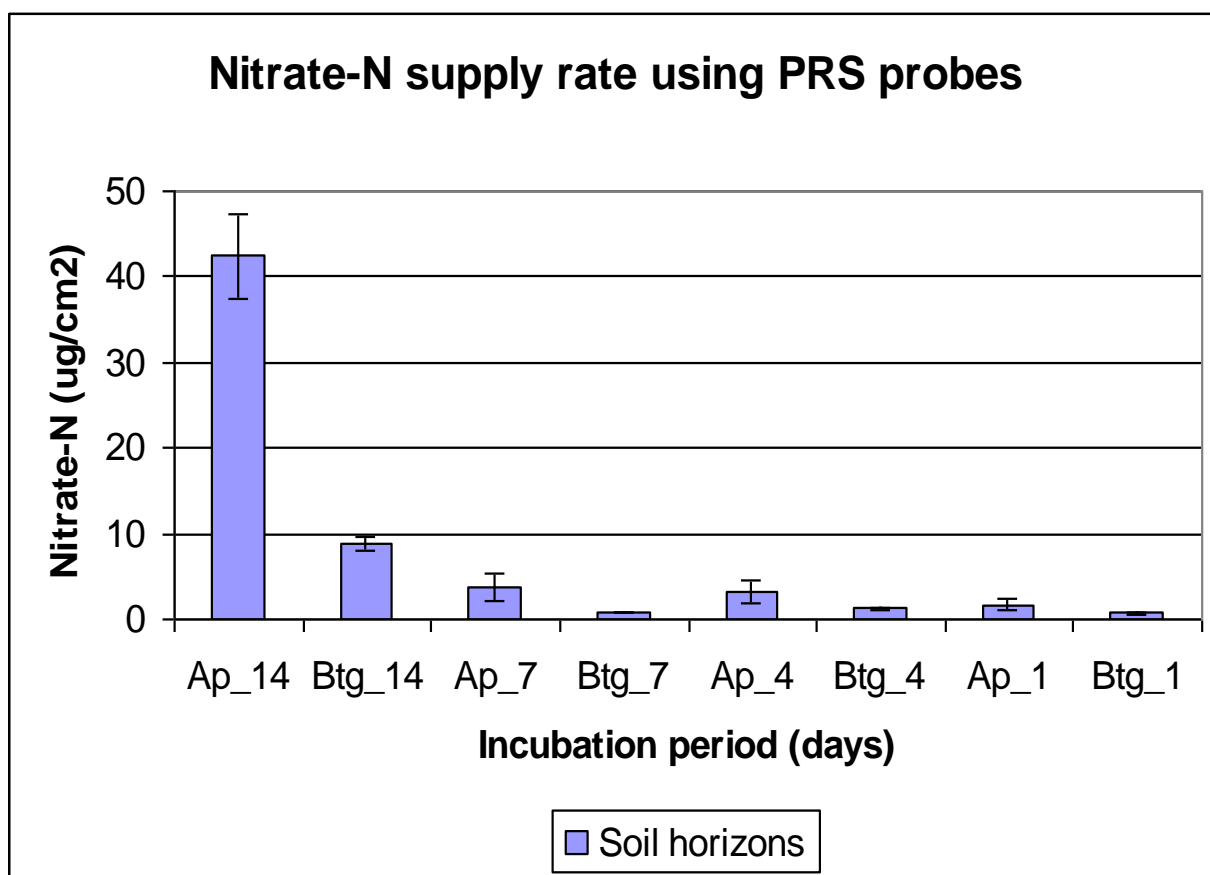
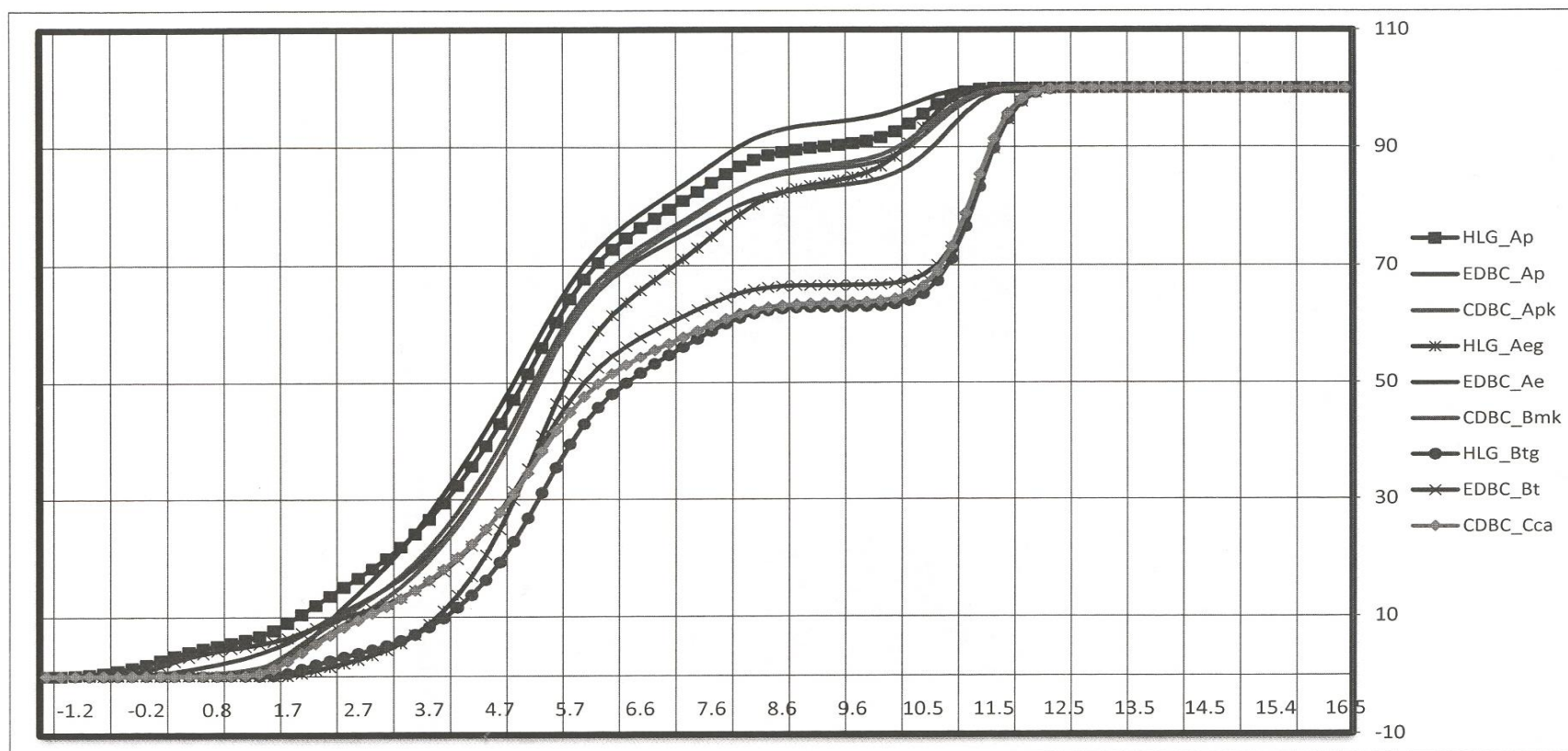


Figure A5.1c N supply rate at different incubation periods

| Appendix 5.2 | | Soils and horizon thickness at SDNWA site | | | | N-0425125 | |
|---------------------|-------|--|----------------|-----------|----------------|------------------|----------------|
| | | Core 1 | | Core 2 | | Core 3 | |
| HLG | | Depth(cm) | Thickness (cm) | Depth(cm) | Thickness (cm) | Depth(cm) | Thickness (cm) |
| | 1 Ap | 0-39 | 39 | 0-42 | 42 | 0-38 | 38 |
| 5150/5251 | Aeg | 39-53 | 14 | 42-58 | 16 | 38-51 | 13 |
| | Btg | 53-100 | 47 | 58-114 | 56 | 51-95 | 44 |
| | 2 Ap | 0-31 | 31 | 0-29 | 29 | 0-40 | 40 |
| 5153/5051 | Aeg | 31-59 | 18 | 29-53 | 24 | 40-60 | 20 |
| | Btg | 59-103 | 46 | 53-107 | 54 | 60-109 | 49 |
| | 3 Ap | 0-15 | 15 | 0-18 | 18 | 0-15 | 15 |
| 5044/5189 | Aeg | 15-33 | 16 | 18-40 | 22 | 15-32 | 17 |
| | Btg | 33-67 | 34 | 40-83 | 43 | 32-77 | 45 |
| EDBC | | | | | | | |
| | 1 Ap | 0-46 | 46 | 0-54 | 54 | 0-48 | 48 |
| 5142/5151 | Ae | 46-65 | 19 | 54-66 | 12 | 48-71 | 23 |
| | Bt | 65-110 | 45 | 66-98 | 32 | 71-105 | 34 |
| | 2 Ap | 0-16 | 16 | 0-20 | 20 | 0-24 | 24 |
| 5146/5056 | Ae | 16-35 | 19 | 20-55 | 35 | 24-75 | 51 |
| | Bt | 35-70 | 35 | 55-100 | 45 | 75-106 | 31 |
| | 3 Ap | 0-32 | 32 | 0-33 | 33 | 0-29 | 29 |
| 5060/5194 | Ae | 32-50 | 18 | 33-50 | 17 | 29-46 | 17 |
| | Bt | 50-84 | 34 | 50-85 | 35 | 46-76 | 30 |
| CDBC | | | | | | | |
| | 1 Apk | 0-15 | 15 | 0-15 | 15 | 0-12 | 12 |
| 5152/5236 | Bmk | 15-60 | 45 | 15-58 | 43 | 12-52 | 40 |
| | Cca | 60-118 | 58 | 58-107 | 49 | 54-110 | 56 |
| | 2 Apk | 0-7 | 7 | 0-9 | 9 | 0-8 | 8 |
| 5165/5039 | Bmk | 7-31 | 24 | 9-54 | 45 | 8-50 | 42 |
| | Cca | 31-87 | 56 | 54-108 | 54 | 50-105 | 55 |
| | 3 Apk | 0-20 | 20 | 0-18 | 18 | 0-20 | 20 |
| 5033/5177 | Bmk | 20-53 | 33 | 18-58 | 40 | 20-54 | 34 |
| | Cca | 53-110 | 57 | 58-106 | 48 | 54-120 | 66 |

Appendix 5.3

75



Cumulative grain size distribution in horizons of three wetland soils at SDNWA